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TEXTILE RESEARCH JOURNAL

VOLUME XVII | October, 1947 | NUMBER 10

PUBLICATION OF

TEXTILE RESEARCH INSTITUTE, INC.

AND

THE TEXTILE FOUNDATION

Editorial Office: 10 East 40th Street, New York 16, N. Y.

TEXTILE RESEARCH JOURNAL

VOL. XVII, No. 10 October, 1947

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TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is the official publication of Textile Research Institute, Inc., and the Textile Foundation.

Manuscripts and communications should be sent to the editorial offices, 10 East 40th Street, New York 16, N. Y.

Subscription rates: General—$10.00 per annum; additional for postage, 50 cents to Canada, $1.00 to all other countries. Special—$5.00 per annum for United States and Canadian students, teachers, educational institutions, public libraries, governmental libraries and departments, plus 50 cents for postage to Canada. Single copies, $1.00 each.

Entered as second-class matter, April 27, 1945, at the postoffice at Lancaster, Pa., under the Act of August 24, 1912.

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TEXTILE RESEARCH JOURNAL

VOL. XVII, No. 10 October, 1947

The Adsorption of Water by Swelling High Polymeric Materials*

Howard J. White, Jr.,† and Henry Eyring ‡

Contribution of the Textile Foundation and the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Abstract

This paper contains a discussion of the water-adsorption properties of a class of long-chain materials with many polar groups, which includes most textile fibers. The process discussed is distinguished from the adsorption by substances such as metal and metallic oxide catalysts in that it is not strictly a surface phenomenon, the adsorbent swelling as water is adsorbed. It differs from simple hydrate formation in that the water uptake is a continuous function of relative humidity, although in theory this behavior can be considered to be caused by the existence of an infinitely large number of possible hydrates. And, finally, it is distinguished from adsorption by liquids by the fact that the adsorbent possesses, and retains during the adsorption process, a certain amount of dimensional stability.

In the first part of the paper a summary is given of some experimental data. This summary is not a complete review of previous work but is rather an outline of the data on the various phenomena associated with the adsorption process. The purpose of this section is to give as much information on the fundamental adsorption process as possible rather than to give data for a large number of representative substances. For this reason many references, especially to chemically modified fibers (which contrast individual members of this class but do not contribute new information on the fundamental adsorption process), are omitted.

In the second section a review of previous theoretical treatments is given and a new theory of the adsorption isotherm for this class of substances is proposed. This treatment is derived by the methods of statistical mechanics and expresses the adsorption isotherm in terms of the relative humidity, regain, and molecular parameters in the simplest case. The application of the theory to experimental data shows surprisingly good agreement between theoretical and experimental isotherms, considering the approximations involved. In some cases missing data are estimated from known data for similar substances.

The third section contains a discussion of adsorption hysteresis in terms of the theory developed here and the theory of absolute reaction rates, as well as a discussion of the constants of the isotherm.

I. Experimental Data

A. Adsorption Data and Terminology

The terminology of sorption varies with various authors. In this paper the general process of the interaction of a substance with atmospheres of different partial pressures of a vapor will be referred to as *sorption*. The take-up of volatile component which occurs on increasing the partial pressure of the vapor will be called *adsorption*. The loss of volatile

* This communication constitutes partial fulfillment by Howard J. White, Jr., of the requirements of Princeton University for the degree of Doctor of Philosophy. It was presented in part before the American Chemical Society, Chicago, September, 1946.

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component occurring on reducing the partial pressure will be termed *desorption*.

The data from adsorption experiments are usually taken either in the form of adsorption isotherms or isosteres. In an adsorption isotherm the amount adsorbed, or regain, is plotted against the pressure of vapor in the surrounding atmosphere at constant temperature. The most commonly used units are grams of vapor adsorbed per gram of dry adsorbent and relative vapor pressure of adsorbate. The relative vapor pressure will be defined as the ratio of the pressure of vapor present to the pressure of vapor over the pure liquid at that temperature. In an adsorption isostere the relative vapor pressure at which a given amount is adsorbed is plotted against temperature, or, quite often, log P against $1/T$. Although isosteres are important to provide data for the determination of the heat of adsorption from the Clausius-Clapeyron equation, the majority of the data are in the form of isotherms, most isosteres being taken from isotherms at different temperatures. This paper will deal almost entirely with isotherms.

All substances in the class to be considered in this paper have a characteristic sigmoid sorption isotherm. At low relative vapor pressures the amount adsorbed increases rapidly with the relative vapor pressure. At moderate relative vapor pressures the increase is smaller and approximately linear. As the saturation pressure is approached the amount adsorbed increases sharply, the isotherm becoming almost parallel to the regain axis. In Figure 1 a typical adsorption isotherm is shown.

The theory of the adsorption isotherm developed in this paper does not limit the volatile component to water specifically. However, since data are scarce on other liquids, only experimental data on the adsorption of water will be considered.

B. Hysteresis

One of the characteristics of sorption isotherms is a rather sensitive dependence on previous sorption history. This sensitivity varies with the adsorbent and the vapor used. Using water vapor, for most fibers the isotherm obtained by placing a dry fiber in atmospheres of increasing relative humidity from zero to unity lies below that obtained by placing a wet fiber in atmospheres of decreasing relative humidity. In other words, for a given fiber sample the regain at a certain relative humidity will be greater for a desorption history than for an adsorption history. This is a general phenomenon for all fibrous materials and is called hysteresis (nylon apparently does not show hysteresis with water vapor [58]). The adsorption and desorption curves obtained as indicated above enclose a certain area, as shown in Figure 6. Apparently any regain at a given relative humidity which lies within this envelope can be obtained by a suitable adsorption-desorption history. For example, let a dry sample be placed in atmospheres of increasing relative humidity up to a relative humidity of 0.5 and then be placed in atmospheres of decreasing relative humidity until it is again dry. The transition to the desorption curve for the wet fiber will not occur instantaneously but, rather, a new desorption curve will be obtained which eventually approaches that for a wet fiber but which for the most part falls between the standard adsorption and desorption isotherms. A standard adsorption isotherm will be defined as one obtained by exposing an initially dry fiber to atmospheres of successively increasing relative humidity, and a standard desorption isotherm as one obtained by exposure of

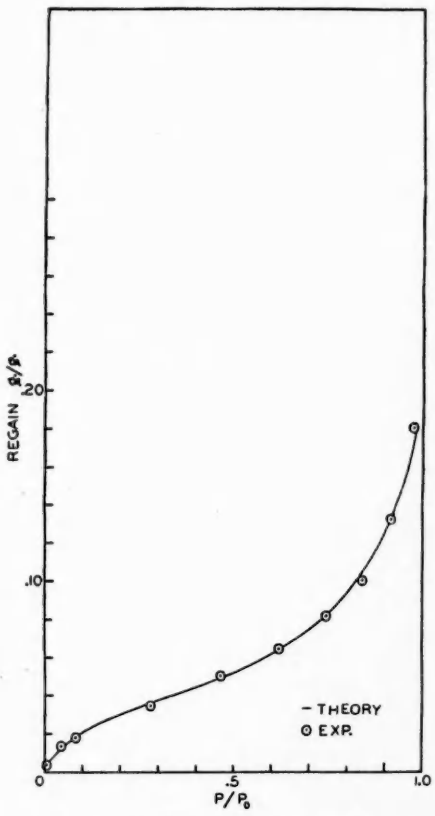

FIG. 1. *Adsorption on cotton using experimental data of Urquhart and Williams* [70].

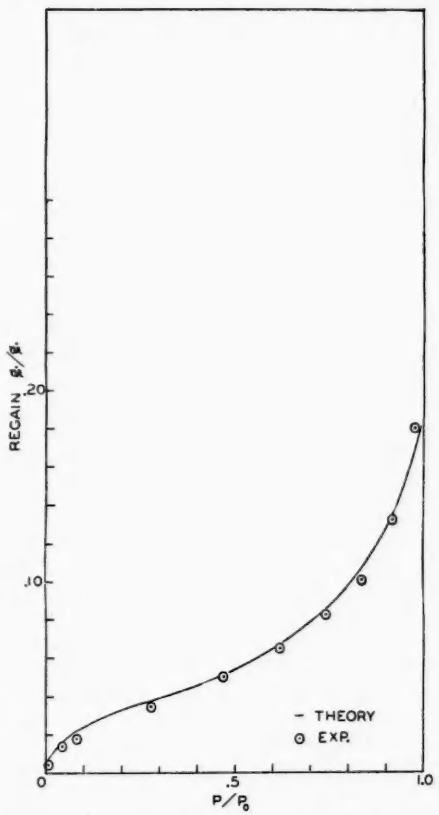

FIG. 2. *Adsorption on cotton using experimental data of Urquhart and Williams [70].*

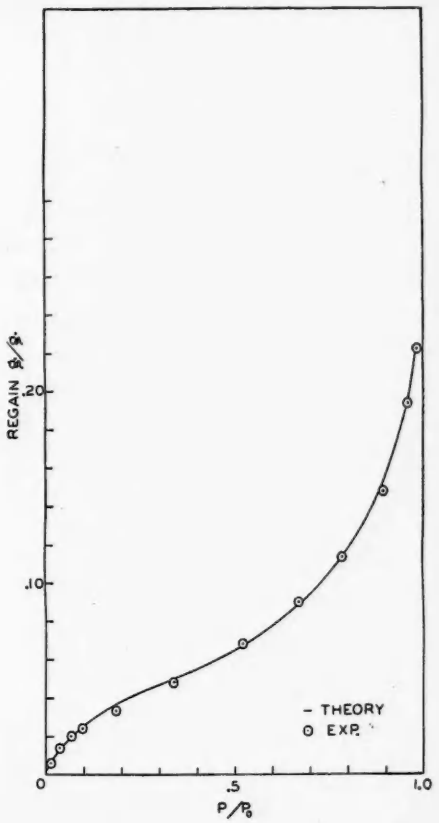

FIG. 3. *Desorption from cotton using experimental data of Urquhart and Williams [70].*

an initially wet fiber to successively lower relative humidities. The initially dry state is reached by drying over P_2O_5 *in vacuo* at room temperature; the initial wet state by immersion in liquid. In some cases exposure to saturated vapor is used to obtain the wet state. Thus at some of the relative humidities there are now three possible values for the regain, depending on the sorption history. Speakman and Cooper [56] have studied this for wool, and Urquhart and Eckersall [67] have also studied this phenomenon for raw and soda-boiled cotton. The results for cotton are similar to those for wool except that the intermediate region between the standard adsorption and standard desorption isotherms is more extended. In other words, on desorbing from an intermediate adsorption value, the standard desorption isotherm for cotton is not reached until much lower relative humidities than those necessary in the case of wool. Data of this type are not extensive enough to make it possible to discuss the laws governing such intermediate transitions across the hysteresis region.

In addition to the dependence of regain on the previous sorption history at a given temperature, the method by which the sample is conditioned influences the sorption isotherms. By conditioning is meant pretreatment to bring all samples to a standard physical state to facilitate comparisons between samples. The rapid rate of regain with increase of relative humidity at low relative humidities, which also implies a high activation energy for desorption, makes it difficult completely to dry a cellulose or wool sample in order to start with a sample at zero regain. For cellulose, drying at 110°C *in vacuo* over P_2O_5 will remove all moisture without decomposing the cellulose [32]. However, prolonged drying at a high temperature alters the physical nature of cellulose, lowering its adsorptive capacity [68, 32]. The effects of varying drying conditions on the adsorption isotherm of wool have been studied by Speakman and Stott [59]. Increasing the temperature of drying decreased the regain at a given relative humidity. However, desorption after saturation in all cases gave the same isotherm so that the effects of drying temperature are apparently removed by complete wetting.

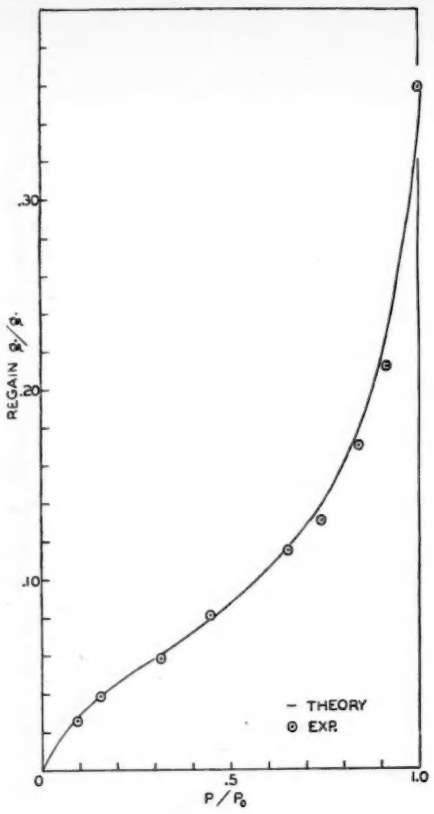

FIG. 4. *Adsorption on jute using experimental data of Macmillan, Mukherjee, and Sen [45].*

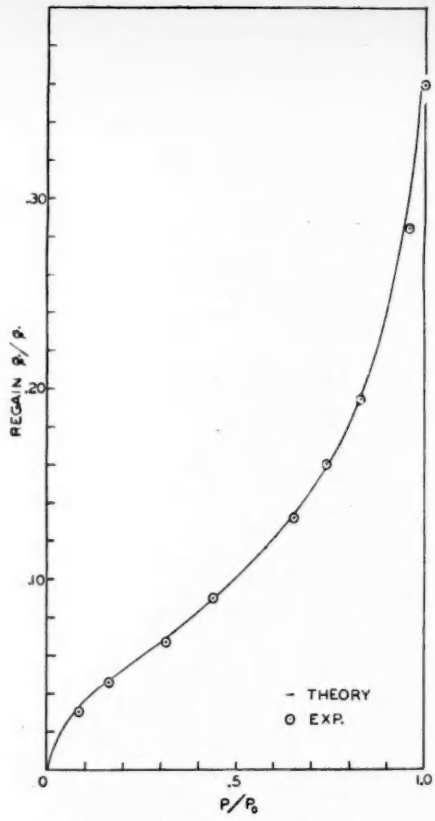

FIG. 5. *Desorption from jute using experimental data of Macmillan, Mukherjee, and Sen [45].*

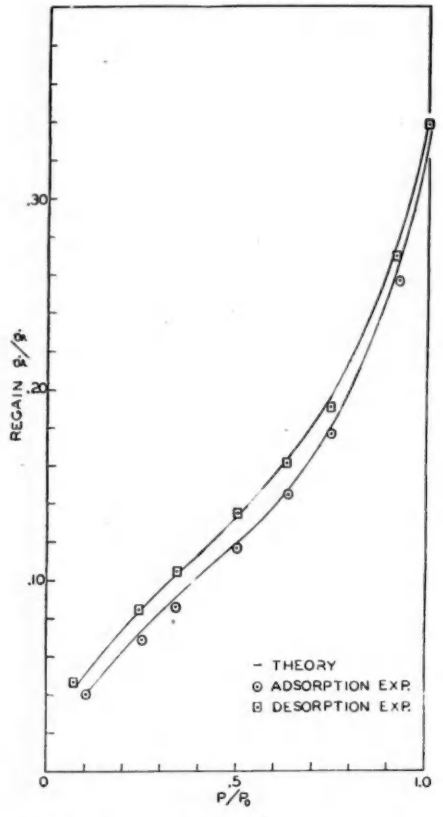

FIG. 6. *Adsorption and desorption for wool using experimental data of Speakman [55].*

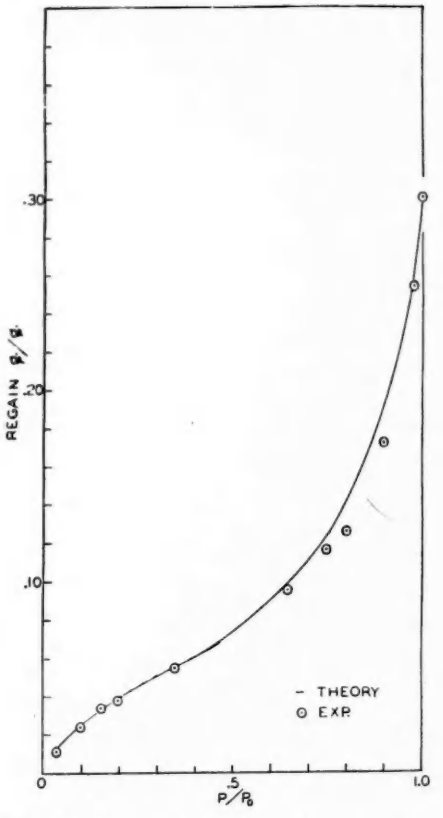

FIG. 7. *Adsorption of silk using experimental data of Goodings and Turl [29].*

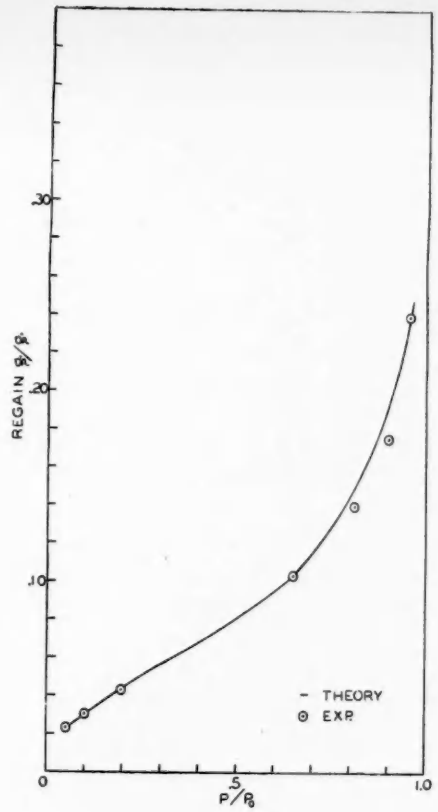

FIG. 8. *Desorption from silk using experimental data of Goodings and Turl [29].*

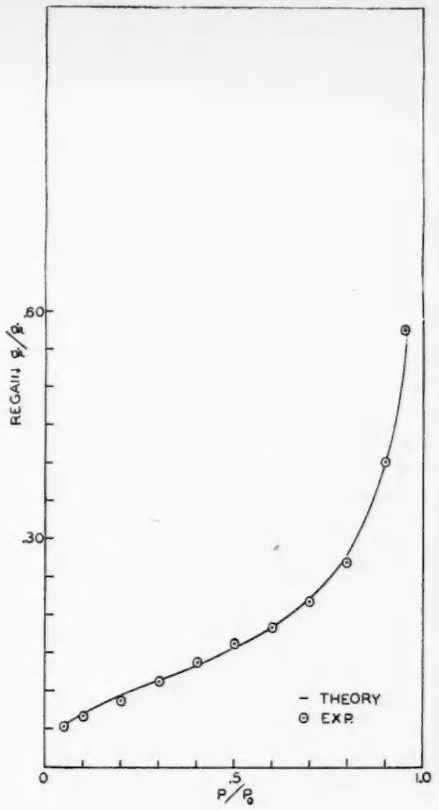

FIG. 9. *Average of adsorption and desorption for gelatin (experimental data of Bull [11]).*

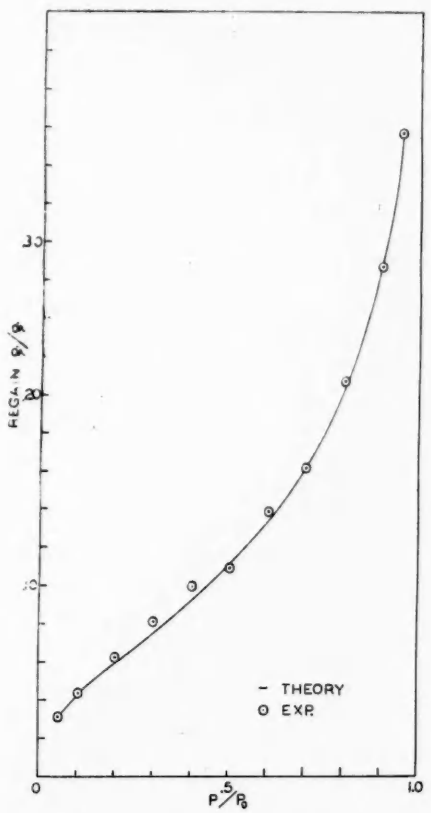

FIG. 10. *Average of adsorption and desorption for serum albumin (experimental data of Bull [11]).*

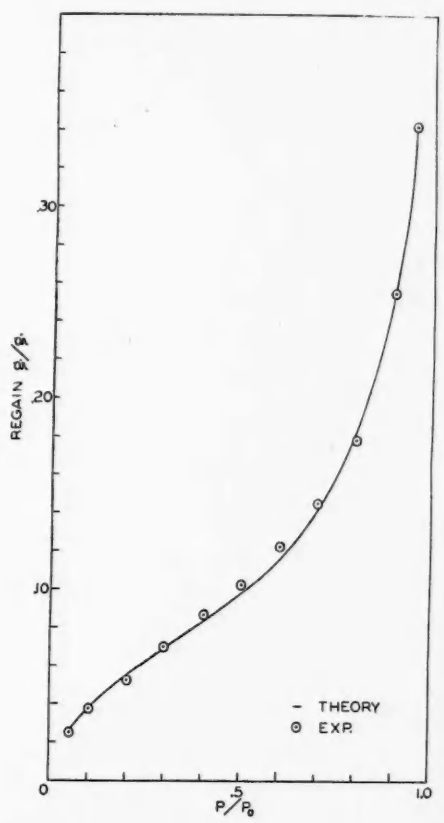

FIG. 11. *Average of adsorption and desorption for egg albumin (experimental data of Bull [11]).*

Heating of wool dried at a low temperature does not lower the adsorption isotherm. Heating at high temperatures (90°C) over water lowers the moisture affinity of wool irreversibly; however, there is some evidence that this treatment causes chemical changes in the wool.

For cotton, heating at 100°C in water increases the regain at a given vapor pressure [66]. Theoretical considerations to be discussed later and the fact that water at 100°C is not known to attack cellulose make it seem probable that Speakman's results were due to chemical changes such as hydrolysis of disulfide linkages. For model filaments [32, p. 6], which are isotropic unstretched cellulose filaments, steaming reduces regain, however, and decomposition is not evident here.

Apparently a process similar to sintering takes place, especially in the presence of moisture. Whether the adsorption increases or decreases after treatment at high temperatures depends on the free energy relationships of fiber and vapor and the initial physical state of the fiber.

The initial drying of raw cotton or cotton which has been scoured gives an irreversible desorption isotherm which lies above the usual desorption isotherm [16, 67]. However, Urquhart [66] found that once the standard adsorption history has been established, repeated adsorption and desorption over the same cycle will give the same hysteresis loops. This effect should be investigated further and will be discussed later.

A discussion of the accuracy and reproducibility of the data is in order here since the idea of several values of the regain at one relative humidity for a single substance is unsound thermodynamically—at least if equilibrium is assumed to be reached in each case. The several regains must thus be produced either by experimental error or by slow-rate processes which make the attainment of equilibrium very slow. The first alternative was advanced by McGavack and Patrick [44], who showed that hysteresis in the adsorption of sulfur dioxide by silica gel could be attributed to the presence of adsorbed permanent gases. This hypothesis was carefully tested for the case of water vapor on cotton by Urquhart [65] and found to be untenable for the hysteresis in this case. Thus some limiting rate process must be responsible for the observed hysteresis. Urquhart and Williams [68] considered weight changes of 0.0003 gram as significant and allowed periods of as long as 2 months in some cases to ensure constant weight. This, coupled with the fact, mentioned before [66], that repetition of a cyclic sorption history (in the one case reported) produces identical isotherms, makes it seem evident that the states produced are metastable states. However, more experimental evidence is necessary before this can be stated definitely.

The ends of the sorption isotherms are difficult to determine experimentally. At the low-pressure end the amounts of vapor taken up are extremely small. Furthermore, it has already been noted that it is difficult to obtain completely dry cellulose or wool without altering the physical nature of the fiber. Hysteresis apparently extends to the lowest humidities measurable, although the differences between adsorption and desorption are very small and hence of doubtful accuracy at the lowest humidities.

At high relative humidities difficulties are encountered because of the rapid rise of the regain with increase of relative humidity and the possibility of an actual condensation of vapor on the fiber. The system also takes a much longer time to reach its apparent equilibrium as measured by the constancy of the weight adsorbed. The amount of water held by cellulose which has been soaked in liquid water and blotted to remove mechanically held excess is greater than the amount adsorbed from the saturated vapor. In the first place, since measurements have all been made on bulk fibers, the packing of the fibers will produce a capillary system between the fibers which is capable of holding water, as has been noted by Urquhart and Williams [69]. However, it is probable that the phenomenon is more complicated than this. Bancroft and Calkin [5] found that centrifuging at high speeds lowered the moisture content below the value obtained from sorption experiments at 100 percent relative humidity. By centrifuging to various moisture contents and then placing the sample (cotton) in a saturated atmosphere, the regain at which the sample neither gained nor lost weight was obtained. The regain obtained in this way was between 27 and 27.5 percent. A sample of the same material was also placed in an unevacuated desiccator over water. The rate of moisture uptake was very slow and unfortunately the experiment was not carried to constant weight. However, the rate of regain is quite small at 25 percent regain, and it seems probable that the constant weight obtained will be below the value obtained by the centrifuge method. It should also be noted that the regain

at saturation for cotton found by Urquhart and Williams [70] is 23 percent, which is considerably smaller although, of course, the samples are not strictly comparable. Moreover, a small difference has been detected between the saturated vapor regain and the regain in liquid water for wool [40], although the evidence is not conclusive. Bancroft and Calkin also cite a similar effect for sheet gelatin obtained by von Schroeder [53]. By suspending a gelatin strip vertically so that part of it was in water and part in saturated vapor, von Schroeder was able to detect greater swelling in the part in the liquid water. He also performed experiments to show that the loss of weight which occurs when a water-swollen strip is put into an atmosphere saturated with vapor was not caused by a gravity-induced mechanical drainage.

The thermodynamic activity of the water is the same in the saturated vapor phase as in the liquid phase. It is, therefore, difficult to conceive of a different equilibrium state in each case. If the process is one of differing rates in bulk liquid and in saturated vapor, the apparent reversibility of the effect which enables it to be repeated by repeated application of water and saturated vapor is hard to explain. The phenomenon has been discussed by Bancroft and others [4, 26] but no satisfactory quantitative theory has been advanced. Furthermore, the experimental evidence is not entirely conclusive. Wolff and Büchner [74] state that small changes in temperature are not rapidly equalized in a large vessel. They claim that if a smaller vessel is used and rigid precautions against temperature fluctuations are taken the von Schroeder effect is not observed.

Cellophane is an ideal substance with which to study this phenomenon. Its lack of macroscopic or morphological complexities and its adaptability for convenient-size samples help to obviate many experimental obstacles in the approach to this problem and should make it possible to take critical data.

C. Permeability and Diffusion

The study of the diffusion of gases and vapors through films of cellulose, etc., can be used to study the mechanism of the interaction of water with the film.

The permeability of high-polymer films has been studied by Barrer [7], Doty [19], and Doty, Aiken, and Mark [20, 21].

There are two possible physical concepts of permeability. The gas can either pass through a set of capillary openings in the macroscopically solid film, as through a porous plug, or the gas can dissolve in the substance of the film and diffuse through it as a gas through a liquid. The experimental evidence seems to support the solution mechanism.

The rate of transfer of vapor across a film of unit thickness per unit area per unit pressure difference is defined as the permeability constant, P. In the proper dimensions this can be set equal to the product of two constants—the diffusion constant, D, which has the dimensions of area per unit time, and the solubility constant, S, with dimensions of volume of gas per volume of polymer [19]. Studies of the temperature variation of permeability show that the following relationships can be set up:

$$P = P_0 e^{-E/RT},$$
$$D = D_0 e^{-E_D/RT},$$
$$S = S_0 e^{-\Delta H/RT}.$$

P and D are rate constants and S is an equilibrium constant for solubility. E is the activation energy for permeation and P_0 is a frequency factor which gives a measure of the entropy of permeation. E_D is the activation energy for the diffusion process and D_0 gives the entropy factor for the activated state for diffusion. ΔH is the heat of solution of the vapor in the polymer and S_0 is an expression for the entropy of solution.

It should be noted that this separation of the permeability constant implies the correctness of the solution mechanism. The separation of the experimental data and the subsequent linear plots of $\log P$ vs. $1/T$, $\log D$ vs. $1/T$, and $\log S$ vs. $1/T$ serve as partial confirmation of the solution mechanism.

Barrer [7] interprets the diffusion process in terms of the theory of holes in liquids. A vapor molecule dissolved in the polymer is at liberty to change its position only when a vacant space or hole is available to it. These holes are produced by changes in the positions of the chains in the polymer network caused by thermal energy.

In the case of permanent gases diffusing through films the activation energy is probably the energy required to form a new hole. If water is diffusing through a film made of chains bearing hydrophilic groups such as $-OH$, strong bonds may be formed between the water molecules and the hydrophilic groups. In this case the breaking of these strong bonds may constitute the major portion of the activation energy.

The influence of plasticizers is also of interest in elucidating the mechanism of the interaction of polymers with vapors. Doty [19], working mainly with polyvinyl chloride, polyvinyl acetate and copolymers, and polystyrene, found that plasticizers changed the heat of solution greatly but did not change the diffusion constant much. The heat of solution is greatly lowered and at the same time the vapor molecules will be much less tightly held.

Work on cellulose films and other materials considered in this paper is scanty. De Boer and Fast [18] have studied the diffusion of hydrogen and air through cellulose and cellulose-derivative films. Regenerated cellulose made by saponifying an acetate film passed 0.95 mm^3 per cm^2 per hour of hydrogen under 1 atmosphere pressure drop. The film was approximately 7 microns thick. The humidity of the hydrogen was not specified but was probably quite low. The film was impermeable to dry air. Similar data obtain for celluloid, which is nitrated cellulose, and cellulose acetate.

Let it be assumed for the moment that all the passage of hydrogen through the cellulose mentioned above is through capillary openings in the film. The openings must be of submicroscopic size since such pores cannot be detected by microscopic examination in regenerated films. Kennard [39] gives the following approximate formula for flow through a tube whose radius is small compared to its length and the mean free path of the gas passed, which is about 10^{-5} cm. for hydrogen at 1 atmosphere:

$$Q_{PV} = \frac{4}{3}(2\pi RT)^{\frac{1}{2}}\frac{a^3}{l}(P_1 - P_2);$$

Q_{PV} = amount of gas passed per sec., given by its PV value;
R = gas constant, cc. atmospheres per degree;
T = absolute temperature;
a = radius of tube;
l = length of tube;
$P_1 - P_2$ = pressure drop across tube.

If the pores are assumed to be 10Å. in radius, the number of pores, and hence the fraction of a square centimeter which is open pore, can be determined. This value is $\sim 1:10^5$. For larger pore radii this value is $\sim 1:10^6$. This is an approximate calculation but gives a maximum value for the possible pore space in dry cellulose films. That the real value lies much below this is shown by the fact that the films are impermeable to dry air.

The exponential dependence of permeability on $1/T$ was also found.

Trillat and Matricon [64] also found cellulose membranes to be impermeable to dry air. In addition they found that the diffusion of air through the cellulose depended strongly on the moisture content. By passing moist air through an initially dry membrane and dry air through an initially moist membrane they showed that the permeability depends on the moisture content of the membrane and that the action of the moisture is reversible.

The passage of solutions through water-swollen cellulose membranes is well known, and it is known that the swelling of the membranes opens pores or, in other words, dilutes the networks so that practical use of the material for dialysis bags or ultrafilters is possible [71].

From this evidence the physical picture of the films is clear. The films consist, when dry, of dense, nonporous polymer networks which do not dissolve permanent gases to any appreciable extent. Water increases the solubility of the gases in the network and also swells and loosens the network to permit more rapid diffusion.

The applicability of this work on films to fibers varies. The general principles of swelling polymer networks should hold true for all fibers and the similarities between films and regenerated fibers should be very close. Natural fibers will be more porous, to varying degrees, because of their structural features, such as lumina.

D. Swelling

It is evident from the preceding section that dry films and, presumably, dry fibers have rather dense, nonporous structures which are greatly changed by water. It is also a well-known fact that water brings about dimensional changes by swelling. To determine a quantitative relationship between the amount of swelling and the amount of water adsorbed it is necessary to know the pore space in the fiber, since water in pores would not swell the fiber.

A priori, measurement of the density and hence of the specific volume of a fiber would seem to be a means of determining the porosity of the fiber. However, unexpected complications arise. The density varies with the immersion fluid used. Using cotton as an example, Davidson [17] found the following densities for native cotton: toluene 1.550, helium 1.567, water 1.6095. This has been interpreted in the following way [71, p. 407]: Helium,

because of its chemically inert nature and small molecular size, is able to penetrate into the smallest crevices and at the same time is not bound to any sites within the network. Hence helium gives the true density. Toluene is unable to penetrate completely into all the crevices in the fiber and hence gives too low a value. Water, on the other hand, can penetrate completely and, in addition, is held on certain sites in the fiber so firmly that the fraction so adsorbed is under considerable compression. For these reasons the density as determined in water is too great. As a proof of the reality of this contraction, Filby and Maass [23] measured the displacement of helium by samples of cellulose of different water contents. They found that the volume of the wet fiber was smaller than the sum of the volumes of the dry fiber and the liquid adsorbed. It was found, furthermore, that the contraction was greatest for the first water adsorbed, finally vanishing after about 8 percent regain. It was calculated that a pressure of 11,000 atmospheres, which is surprisingly high, would be required to produce a similar compression in liquid water.

P. H. Hermans [32] interprets these density data in a different fashion. He points out that the concept of density loses meaning when applied to substances containing holes of molecular dimensions where the dimensions of the molecules of the immersion fluid may be a significant factor. He considers the density given by inert liquids such as toluene, benzene, etc. (which all give the same value for the density) as the density in the usual macroscopic sense. The higher value in water is caused by the ability of certain parts of the fiber (see section IE) to form a homogeneous molecular dispersion with water. The apparent volume contraction is brought about by the more efficient mixing of cellulose and water molecules which this dispersion brings about. By this picture the true density is given by the value in water. No particular significance is attached to the value in helium although it could be equally well used to give the apparent macroscopic density.

This interpretation of the facts is more plausible than the first and does not require the large pressures which must be postulated if the contraction is considered to be real.

It should be noted that density measurements at various regains can be used as a criterion of swelling only if it is proved that there are no capillary systems in the fiber. However, direct measurements are necessary if it is suspected that pores exist. The ease and accuracy with which these direct measurements are made depend on the fiber used. If the fiber is uniform and has a circular cross section, the measurements are quite accurate. In general, artificial and regenerated fibers are much more uniform and regular in cross section than the natural fibers. P. H. Hermans [32] has made experimental isotropic regenerated fibers and has found that direct measurements and density measurements agree within the accuracy of the experiments. From these and other experiments he concludes that regenerated fibers do not contain capillary systems.

Natural fibers usually are less regular than regenerated fibers. Wool apparently has a scaly outer surface; cotton is in the form of a flat, twisted ribbon. Often, central channels or lumina are present. Finally, variations between individual fibers are apt to be greater.

There is, however, a qualitative correspondence between regain and swelling. Clayton and Peirce [14] found a volume increase of 34 percent for an average on 8 soda-boiled cotton fibers. This corresponds to a weight increase of about 22 percent, assuming a density for cellulose of 1.6 and for water of 1.0. This is in approximate agreement with values found by Urquhart and Williams [68].

Collins [16] has examined the swelling of cotton in air of various relative humidities. Data are given showing regain, percentage change in cross-sectional area, and percentage change in length as functions of relative humidity for both adsorption and desorption. From these data he obtained the ratio of observed swelling to that calculated on the assumption that the water added increased the volume by its normal specific volume. From a statistical analysis of the deviations from the mean of the values at the various humidities, he concluded that the results were incapable of yielding quantitative information on the deviation of the apparent specific volume of the adsorbed water from the normal value. It was also concluded that the hysteresis shown in the length measurements was not certain but that the hysteresis of the area measurements is definitely real. It should be further noted that the area curve shows roughly the same shape as the regain curve, as well as the hysteresis.

Hermans [32], from comparison of density measurements on ramie in benzene with microscopic measurements of the volume of the fiber wall of

ramie [27], concludes that the pore volume in ramie amounts to 10 percent. He also notes that comparison of density measurements in benzene with direct swelling measurements at various regains for cotton indicates that the swelling at low regains is greater than the volume change. This is probably the result of inaccuracies in the direct measurements caused by changes in shape of cotton fibers with increase in moisture content. The dry fiber is a flat ribbon, whereas a soaked fiber is round.

To summarize—artificial fibers apparently do not have any permanent capillary space in them. Natural fibers probably do have some capillaries but it is evident from Collins' work that the amount of water condensed in these capillaries and hence not contributing to the swelling is small. There is also some evidence that some of the first water molecules adsorbed do not contribute their entire molecular volume to swelling. This fraction is small and its exact amount is difficult to determine. The assumption will be made later in this paper (see section IIB) that each water molecule adsorbed contributes its normal molecular volume to swelling. It is seen here that this is a first approximation. The error introduced in this way is small but its exact value is uncertain.

One further result of Collins' work should be noted. The change in diameter of a cotton fiber is greater than the change in length. This phenomenon is general and a correlation has been drawn between the anisotropy of swelling and orientation of molecular chains along the fiber axis.

P. H. Hermans and de Leeuw [33; *see also* 32, p. 6] have formed isotropic model filaments of rayon by extruding viscose through a capillary at low pressures and no stretch into a salt or acid bath at room temperature. These fibers show isotropic swelling. Oriented fibers were formed by stretching the isotropic xanthate filaments and decomposing the xanthate to cellulose. These fibers are anisotropic, showing orientation along the fiber axis as revealed by x-ray diffraction patterns, and show anisotropic swelling.

X-ray pictures of swollen fibers also give data on the homogeneity of swelling. This has been extensively considered by Katz [38]. There are three possibilities. The x-ray diagram of the fiber may remain unchanged in spacing and intensity except for a slight increase in the amorphous background. In this case the vapor is unable to penetrate into the crystalline regions of the material and the adsorption is heterogeneous, taking place only in the unoriented regions. Cotton in water is an example of a fiber showing this behavior. The fiber diagram may change continuously as swelling occurs, indicating that the crystalline as well as the amorphous regions are taking up water. The relative spacings within the crystal may even remain constant for a considerable range of swelling. Several crystalline proteins exhibit this type of swelling. Finally, the original fiber diagram may gradually decrease in intensity and be replaced by a new one as swelling proceeds. This can be caused by the formation of a new compound which has formed through interaction with the swelling vapor or by a physical rearrangement induced by the swelling substances. The process of mercerizing cotton is an example of this last type of swelling.

Which type of swelling occurs depends on the individual characteristics of the adsorbent and the adsorbate. This point will be discussed for each substance separately as various isotherms are considered.

E. Relationship of Adsorption to Other Properties

In addition to hysteresis and swelling, which are integral parts of the phenomenon, other properties are greatly influenced by the moisture regain of a given fiber. Studies of other properties give added knowledge of the mechanism of adsorption, in addition to being of great importance in their own right.

The most commonly studied and technically important properties of a fiber are its mechanical properties, and these are strongly dependent on the fiber's humidity condition.

In general, the wet strength of a fiber is lower than its dry strength and the elongation at break is greater for the wet than for the dry fiber. For cotton, both the breaking strength and the elongation at break increase with increasing relative humidity [9], although regenerated cellulose fibers follow the general rule. It has been suggested that moisture decreases the number of secondary intermolecular bonds and also allows the stress to be more uniformly distributed. The relative importance of these two effects would determine whether the wet strength decreased or increased. The stress at which a fiber yields and breaks the linear relationship between stress and strain decreases as the relative humidity increases, and the elongation at a given stress increases with relative humidity on the conventional stress-strain plot.

Data on the relation of mechanical properties to regain have been taken primarily by investigators interested in elucidating the mechanism of the fiber's mechanical responses. However, they are also an as yet untapped source of information about the mechanism of the fiber-vapor interaction.

The electrical properties of fibers also change with relative humidity. The resistance of a fiber plotted as a function of relative humidity looks roughly like an inverted adsorption isotherm, the resistance decreasing with increasing relative humidity [47]. The resistance depends on the regain and if resistance is plotted against regain the hysteresis disappears. Data on the dielectric constant of cotton at various regains give further information on the way in which water is held by the cellulose. The values at low regains indicate that the adsorbed water is held in fixed positions with about the freedom that would obtain in ice. As the regain increases, the incoming water is less firmly held, finally having the freedom of liquid water. The question of how the water is held on the cellulose will be considered further later in the paper.

The optical properties of fibers and their dependence upon regain have been extensively discussed by Hermans [32]. Density determinations such as those discussed in section ID can be checked with optical data. Of more value in discussing the mechanism of adsorption are the data correlating swelling anisotropy with molecular orientation through optical anisotropy. X-ray evidence on fibers showing increasing anisotropy of swelling also indicates increasing orientation, which, in turn, shows that the swelling anisotropy is attributable to geometrical causes.

The thermodynamic properties of fibers are all dependent on the regain and give much information on the adsorption process. They will be discussed in the next section.

F. Thermodynamics of Sorption and Swelling

Adsorption on a nonporous swelling adsorbent is similar in several respects to solution in a liquid. In fact, the plot of amount dissolved versus relative humidity for sulfuric acid shows the same sigmoid behavior that is typical of the adsorption isotherms considered here. It is possible to apply a thermodynamic treatment to sorption or swelling which is similar to that applied to dilute solutions. This has been done by J. R. Katz and others and is conveniently presented in various reviews [38, 61].

One important complication occurs in the application of thermodynamics to the sorption process. The laws of thermodynamics which will be used here apply strictly only under equilibrium conditions. In adsorption experiments the experimental source of data and the standard of reference for comparison is the isotherm. Because of hysteresis effects this varies with sorption history. Strictly speaking, therefore, the thermodynamic equations should be applied only to some intermediate isotherm which could be found by waiting an infinitely long time at every relative humidity. This isotherm would give the same regain for a given relative humidity regardless of the previous condition of sorption of the sample. In lieu of this experimentally impossible procedure some authors average adsorption and desorption data in an attempt to approximate the equilibrium conditions. Others assume that no major change in the character of the isotherm occurs on going from the standard adsorption to the equilibrium isotherm and that thermodynamic values obtained from the adsorption isotherm will be of the correct order of magnitude. At the present time either method is probably acceptable since the data are used to give information on the adsorption process rather than in strictly quantitative calculations. They will not be differentiated in this paper. One further difficulty occurs in the case of substances which do not possess a three-dimensional network. In this case the true equilibrium regain may correspond to a dilute solution, in which event the standard isotherms may differ considerably from the equilibrium isotherm. For this reason the high-regain end of the isotherm should be avoided in discussing the thermodynamics of the swelling process. Strictly speaking, only three-dimensional stable networks should be considered.

As in the thermodynamics of solutions, there are two generally used values of heat—free energy and entropy; the differential value and the integral. To use the heat of adsorption as an example, the differential heat of adsorption at the regain α is the heat produced when an infinitesimal amount of water is adsorbed by a gel of regain α.

The integral heat of adsorption for the regain α is the total heat produced when 1 gram of dry gel adsorbs enough water vapor to bring it to the regain α. The heat of adsorption and the heat of swelling are related by the equation

$$\Delta H_A = \Delta H_S + L,$$

where ΔH_A is the heat of adsorption, ΔH_S is the heat of swelling, and L is the latent heat of vaporization of water, all for the same amount of water. Thus swelling refers to liquid water and is generally discussed because of its convenience.

It is difficult to measure integral values directly for intermediate water contents. Therefore, gels of a given water content, α, are put in liquid water and the amount of heat developed is obtained. These values are heats of wetting of gels of given regains. Subtraction of these values from the heat of wetting of the dry gel gives integral heats of swelling. Differential heats of wetting can also be used. The differential heat at a given regain may be determined by taking the slope of the curves produced above or from the temperature dependency of adsorption.

The data in Table I are taken in part from a table of Hermans [32, p. 38]. W represents the integral heat of swelling obtained by putting fibers of moisture content α in water and measuring the heat of wetting, and w represents the differential heats of swelling taken from a plot of these by graphical differentiation. The experimental data for cotton were taken by Argue and Maass [1]; those for rayon were taken by Hermans [32]. The values of the differential heats are those of Hermans obtained graphically and are slightly different from those given by Argue and Maass, who obtain them by differentiating an empirical relation for the integral heat.

The integral heat of wetting for cotton is 10.16 calories per gram dry fiber and that for viscose rayon is 22.4 cal./g.

The integral heat of swelling increases rapidly at first and approaches a limiting value. The differential heat of swelling is greatest at zero regain.

One further fact should be noticed. The integral heat of wetting of viscose rayon is double that of cotton, but the differential heats at zero regain are the same for the two materials. This suggests that the initial process of water adsorption is the same for the two types of cellulose but that viscose rayon has more active groups per gram than cotton.

The maximum differential heat of swelling as determined by Argue and Maass varied from 250 cal./g. to 280 cal./g. Neale and Stringfellow [48], using the indirect method on low-regain cotton, obtained a value of 280 cal./g.

Katz [38] found that the integral heats for a number of gels, including cellulose and casein, could be represented by the empirical formula

$$W(\alpha) = \frac{A\alpha}{B + \alpha},$$

where A and B are constants. This equation is also valid for sulfuric acid. For a series of 6 different gels the differential heat at zero regain varied from 250 cal./g. to 420 cal./g.

Apparently the initial adsorption process produces about the same amount of heat in many cases, suggesting that the same general reaction occurs. The total heat produced on wetting varies considerably from fiber to fiber, but the fact that the integral heats can often be expressed by the same empirical formula indicates that the processes are similar in type although different in quantity.

For systems in which the work done against the atmosphere is small compared to the internal energy changes, the free energy and the work function can be set equal. This is clearly the case for a swelling gel from a consideration of the large heat changes discussed in the previous paragraphs. The change in the work function of 1 gram of a vapor treated as an ideal gas expanding isothermally from the pressure P_0 to a pressure P_α is

$$\Delta A = \frac{RT}{M} \ln \frac{P_\alpha}{P_0}.$$

If the vapor is adsorbed by a solid, the relative vapor pressure and the amount adsorbed are connected by the experimentally determined adsorption isotherm. At equilibrium the partial molal free energy change of the vapor on going from the vapor

TABLE I

	Cotton		Viscose rayon	
α	W $\frac{\text{cal.}}{\text{g. dry cellulose}}$	w $\frac{\text{cal.}}{\text{g. water}}$	W	w
0.0	0.0	232	0.0	235
.005	1.16	216	1.1	226
.01	2.16	194	2.3	216
.02	3.99	159	4.4	195
.03	5.26	125	6.4	175
.04	6.38	95	8.0	155
.05	7.18	69	9.4	137
.06	7.77	48	10.7	121
.07	8.17	33	11.9	104
.08		24	12.8	89
.09			13.6	73.5
.10			14.2	58
.11			14.7	47
.12			15.1	37.5
.15			16.1	26
0.19			16.9	16.5

to the adsorbed state is zero. The same reasoning applies to vaporization of 1 gram of liquid in equilibrium with the vapor. Therefore if P_0 is the vapor pressure of the pure liquid at a given temperature and P_α is the pressure of the vapor over an adsorbent which is at regain α, the free energy change of 1 gram of liquid adsorbed by an infinite quantity of adsorbent of regain α is that given in the equation above.

If the process is to be carried out isothermally and reversibly, a pressure π must be applied to the gel at all times so that a slight increase in the pressure will reverse the adsorption process. This pressure is known as the swelling pressure and πv, where v is the volume change of the gel on adsorption, is also an expression of the free energy (see, however, the work of Barkas [6]).

It will be noted that the free energy of swelling given above is a differential free energy change. An integral free energy change for the addition of α grams of water to 1 gram of dry gel can also be defined and determined in the same way as the integral heat change. By the use of the Gibbs-Helmholtz equation the differential or integral entropy change on adsorption can be determined:

$$\Delta F = \Delta H - T\Delta S.$$

Stamm and Loughborough [60] have determined the differential heats and free energy changes for Sitka spruce pulp from their own data and also for cotton from the data of Urquhart and Williams [70]. The free energy changes were calculated from the 50°C isotherm; the heats, by plotting $\log P/P_0$ against $1/T$ for constant regain. The 40°C and the 60°C values were used in this case.

The free energy change is smaller than the heat change and hence there is a decrease in entropy when 1 gram of water is added to an infinite amount of gel of moisture content α. The $T\Delta S$ value at zero regain is about the same as the latent heat of fusion of ice and, therefore, the first water molecules adsorbed can be considered to be attached to fixed sites and oriented to about the same extent as ice. As the regain increases, the differential entropy change decreases. Since the heat of adsorption apparently is very small at higher regains and the free energy change must become zero for the regain in equilibrium with liquid water, the final water molecules adsorbed must be very close thermodynamically to liquid water.

The unexpected magnitude of the differential heat of swelling and the large entropy decrease at zero regain show that the initial reaction is similar to the formation of primary chemical bonds. The energy of formation of a hydrogen bond is about 280 calories per gram of water. However, the heat of adsorption is the net of the heat of formation of the bonds formed minus the heat of formation of the bonds broken. Therefore, if hydrogen bonding is to be the cause of the heat of adsorption, twice as many bonds must be formed as are broken. Neale and Stringfellow [48] suggest that there are unsaturated hydrogen bonding sites in the amorphous areas of the cotton and that the first water molecules adsorbed are held to two neighboring sites by strong hydrogen bonds, the extra hydrogen bond accounting for the large heat change.

One further point can be cleared up at this time. One of the earliest theories of gel adsorption was the capillary theory. In its pure form it may be stated as follows: The vapor pressure over a surface depends on the curvature of the surface which in turn depends on the radius of the tube in which the water is contained; the smaller the radius, the lower the vapor pressure with which the water in the tube is in equilibrium. The equation connecting these quantities was derived from classical considerations by Lord Kelvin and it is doubtful that it is valid in pores of diameter too close to the molecular radius of water. Waiving this possible objection, there are still other more serious difficulties.

Diffusion and density experiments and direct examination of swollen fibers under the microscope bear evidence against the existence of any permanent system of pores of any great magnitude. Furthermore, no capillary condensation theory can account for the large initial heat and entropy changes in the sorption process, for in this case both the heat and the entropy changes should be similar in magnitude to those for condensation. Finally, there is the specificity of the sorption process—for example, in the case of cellulose the large uptake of water and the small uptake of benzene, in the same relative vapor pressure of each, indicate that adsorption is, at least partially, a case of chemical interaction rather than of physical condensation.

The swelling pressure has already been mentioned in discussing the free energy of swelling. It can be given by

$$P = -\frac{RT}{MV}\ln\frac{P}{P_0}.$$

This equation is identical in form with one which

can be derived for osmotic pressure. The explicit derivation of the swelling pressure can, in fact, be made by using analogous arguments to those used in deriving the osmotic pressure of dilute solutions. It is therefore interesting to know the relationship between osmotic and swelling pressures. They can both be considered manifestations of the same phenomenon. Osmotic pressure is the experimental demonstration of swelling pressure through the use of an artificial semipermeable membrane for substances which dissolve or are in solution. In the case of a swelling body the substance itself acts as its own semipermeable membrane. The experimental van't Hoff formula, $P = RTC_0$, where C_0 is the concentration of the dissolved substance in moles per liter of solvent, is not obeyed by swelling bodies. Rather, an equation $P = P_0C_0^n$, where n is often equal to about 3, is found to hold. This can be rationalized by considering the osmotic pressure to which van't Hoff's relation applies and swelling pressure as occurring in different concentration ranges, the intermolecular forces in the case of swelling rendering the van't Hoff relation invalid. (See Steinberger [61] for a discussion.)

G. Effects of Temperature on Adsorption

The influence of temperature on adsorption and swelling presents a number of interesting phenomena which are as yet unexplained. Mention has already been made of the use of values of relative humidity at various temperatures over samples at a given regain to determine heats of swelling. However, the regains covered have been very low and the temperature ranges small. For larger regains and over greater temperature ranges the plots of $\log P/P_0$ against $1/T$ are not straight lines, showing that the heat of swelling at a given regain is temperature-dependent.

The most extensive study of the influence of temperature (from 10°C to 110°C) on swelling was made by Urquhart and Williams [70] on cotton. They found that the regain at a given relative humidity decreased as the temperature increased and that the isotherms had roughly the same shape below 60°C. Above 60°C the regain at a given relative humidity decreased below about 88 percent relative humidity and increased above this value. In other words, the isotherms curved up more sharply at the higher humidities for higher temperatures and crossed. If regain is plotted against temperature for various relative humidities, a minimum regain occurs at the higher relative vapor pressures, the minimum coming at lower temperatures as the relative humidity increases. It should also be noted that the values at 110°C suggest that the regain is again starting to decrease. It was also found that hysteresis decreases with an increase in temperature, becoming very small in the vicinity of 100°C.

Wiegerink [73] also studied the effects of temperature on the sorption isotherms for a number of materials, among them cotton. The work covered temperatures from 96°F to 302°F; however, the apparatus was such that vapor pressures of greater than 1 atmosphere could not be used. As a consequence, relative humidities of more than 80 percent were not used in the higher temperature ranges, and the crossing of the isotherms found by Urquhart and Williams could not be verified.

Supplementary evidence of the correctness of the crossing of the isotherms is supplied by some work by Collins [16]. Cotton fibers were placed in small glass cells with water and put in a miniature temperature bath on the stage of a projection microscope. The diameter of the fibers was measured at various temperatures. A minimum swelling was obtained in the vicinity of 50°C. Data are given on regain area and swelling as determined by specific volume from the work of Davidson [17]. These values from Davidson's work are fractions of the volume of swollen cotton at 15°C. They are obtained indirectly from considerations of the specific volumes in helium and in water and are hence subject to the criticisms given in section IC. The regain values are extrapolated from the isotherms of Urquhart and Williams [70]. The changes in length were so small and so irregular that they could not be accurately measured. It is, therefore, possible to use the area change as a swelling change. The three curves are all roughly of the same shape and show a pronounced minimum in the vicinity of 50°C and a maximum (for area and regain) at about 100°C. Collins also states that one sample was taken to 200°C, when the observed swelling was less than 5 percent. Speakman and Cooper [57] have studied the isotherms of wool at various temperatures. The problem is complicated in the case of wool by a probable slow hydrolysis of disulfide linkages by water at more than 55°C. However, the same phenomenon found for cotton at about 60°C applies for wool at a lower temperature. Plots of amount adsorbed against temperature at a given

relative humidity show a linear decrease at lower relative humidities and a minimum at higher values in the vicinity of 45°C. This correlates with the fact that other important properties of wool have minima or maxima at this same temperature.

II. Theories of Adsorption

A. Review of Previous Work

To be satisfactory for the class of materials of interest here, a theory of adsorption must account for all of the facts given in part I in so far as they apply to the particular fiber. Fibers are specified rather than gels because rubbers have adsorption and swelling properties which are quite different.

The salient features which any theory must account for are the following. The first water molecules to be adsorbed are taken up with a large evolution of heat and a decrease of entropy which indicates strong bonding. This is reflected by the rapid increase of regain with humidity at low relative humidities. As the regain increases the heat and entropy changes are smaller, eventually approaching those for condensation to liquid water. The rate of change of regain with relative humidity decreases in the middle range of relative humidities but increases to a large value as the relative humidity approaches 1.

Swelling occurs throughout the adsorption. The evidence is inconclusive but to a first approximation every molecule can be considered to contribute to an equal degree to the swelling, although a closer approximation would take account of the fact that some of the water molecules first adsorbed do not contribute as much to the swelling.

The cause of the standard hysteresis effect must be explained and, in addition, the changes in the adsorption isotherm which can be brought about by heating must be interpreted.

In general, the various theories of adsorption and swelling can be divided into two groups, the first group treating the adsorption as a taking up of water on a surface and the second as a solution in a viscous medium.

In the first case the adsorption is considered to be a heterogeneous process. The fiber is considered to have a large amount of internal surface. There are residual valences on these surfaces which can strongly adsorb water. The amount of surface can be altered by changes in swelling or temperature changes. These assumptions account for the various hysteresis phenomena, since changes in the surface area would change the amount adsorbed at a given relative humidity. The surface area can be altered only over a limited range and, because of the residual valences on the surfaces, there exists a surface of minimum free energy for the dry fiber so that the properties of the fiber cannot be changed indefinitely. Urquhart [66] was the first to develop the above picture completely.

In the second case the fiber is assumed to be divisible into ordered and unordered regions. Adsorption is considered to be the solution of water in the unordered regions. There are sites of strong adsorption in the unordered region, just as there are in sulfuric acid, and mixing of the unordered region with water is considered in many ways to be analogous to dilution of sulfuric acid.

Hermans [32] has recently discussed adsorption from this standpoint. Evidence from x-ray data is cited for the existence of two hydrates, the formulas of which are either $C_6H_{10}O_5 \cdot \frac{1}{3}H_2O$, $C_6H_{10}O_5 \cdot 1\frac{1}{3}H_2O$; or $C_6H_{10}O_5 \cdot \frac{1}{2}H_2O$, $C_6H_{10}O_5 \cdot 1\frac{1}{2}H_2O$. The first hydrate is formed from cellulose II, which is the crystalline form found in regenerated and mercerized fibers. The other hydrate is found only when alkali cellulose or cellulose xanthate is decomposed at low temperatures, and is unstable at room temperature as a crystalline form going to the first hydrate. It should be noted that water is considered to penetrate and swell the crystalline sections of mercerized and regenerated fibers but not native cotton fibers.

There are two possible hydrates for each glucose residue. Thus a long-chain molecule made up of glucose residues has a large number of hydrates and could give a continuous adsorption isotherm such as is found experimentally. The final rise of the isotherm at high humidities can be attributed to weakly held multilayers or capillary condensation.

Peirce [52] introduced the concept of strong and weak bonding sites on the surface into a theoretical treatment, but made the tacit assumption that there is no interaction between a weakly adsorbed molecule and an adjacent strongly adsorbing site.

Babbitt [3], for cellulose, and Bull [11], for proteins, have discussed the adsorption of water on the basis of the Brunauer-Emmett-Teller theory of adsorption [10]. This is a theory of multilayer adsorption. The molecules adsorbed in the first layer are considered to be bound to the adsorbent with a binding energy E_1. The molecules in subsequent layers are considered to be in the liquid state and

give off the heat of condensation E_L on adsorption. For an adsorbent on which only a limited number of layers can be adsorbed the adsorption isotherm is given by

$$\frac{x}{m} = \frac{\left(\frac{x}{m}\right)_S Cy}{1-y} \cdot \frac{1-(n+1)y^n + ny^{n+1}}{1+(c-1)y+cy^{n+1}},$$

where x/m is the regain in grams adsorbed per gram of adsorbent, $(x/m)_S$ is the regain when the entire surface is covered with a monolayer,

$$y = \frac{P}{P_0}, \quad C \cong e^{\frac{E_1 - E_L}{RT}},$$

and n is the maximum number of layers which can be adsorbed. n is interpreted as being a function of the width of the pores within the adsorbent which limit the adsorption at saturation. If the surface is a free surface, $n = \infty$ and the isotherm can be cast into the form

$$\frac{P}{\frac{x}{m}(P_0 - P)} = \frac{1}{\left(\frac{x}{m}\right)_S C} + \frac{C-1}{\left(\frac{x}{m}\right)_S C} \cdot \frac{P}{P_0}.$$

For an adsorption obeying this equation, a plot of $\frac{P}{\frac{x}{m}(P_0 - P)}$ against P/P_0 should give a straight line. Such a plot deviates rapidly from a straight line after $P/P_0 = 0.5$ for the case of water adsorbed on cellulose or proteins. However, if the deviations are assumed to be due to finite pore size, it is possible to use the linear portion of the plot in the low relative humidity region, where the influence of the size of the pores is small, to evaluate the constants $(x/m)_S$ and C for use in the three-constant equation. In this case the theoretical curve was found to deviate markedly from the experimental data at relative humidities greater than 0.7, where, again, capillary condensation is assumed to take place. No theoretical expression for the capillary condensation is given. A more serious difficulty in any explanation of this type lies in the fact that no explanation is given for the swelling which occurs on moisture take-up. A substance obeying the above theory would, if anything, shrink slightly because of the surface forces of the liquid in the pores.

So far no consideration has been given to the possible influence of swelling on the adsorption isotherm. It is obvious that the network structure of the swelling gel will resist the deformations brought about by the adsorption of liquid. Barkas [6] considers the effects of gel structure on swelling pressure and on hysteresis. Sorption in a swelling gel is considered analogous to sorption in a solution under pressure. The solution tends to increase in volume because of the liquid adsorbed and at the same time tends to decrease in volume, depending on the external pressure and the bulk modulus of the liquid. In a gel, swelling is resisted according to the bulk modulus of the gel substance and hence, depending on the degree of swelling, the adsorbed liquid will be under a different hydrostatic pressure. In addition, a gel is capable of resisting swelling because of its rigidity. The gel has a certain modulus of rigidity, and if the swelling is such that the gel will be deformed in shape, a term will be introduced in the work of swelling depending on this modulus, in addition to the purely compressive term. This rigidity factor may be caused by external constraints such as a confining cylinder, or by internal factors in the gel structure which tend to produce anisotropic swelling.

Barkas' equations indicate that if the shear-resistance forces are such that a frictional type of dissipation of energy occurs on swelling, hysteresis will occur in the sorption cycle. In other words, if the gel structure is altered in an inelastic fashion by the swelling, hysteresis will occur. Barkas offers no molecular mechanism for this inelastic shear.

Cassie [12] applies the Brunauer-Emmett-Teller isotherm to wool, making use of the work of Barkas. The hydrostatic pressure caused by the swelling of the gel raises the relative vapor pressure of the adsorbed liquid. Since the Brunauer-Emmett-Teller isotherm applies only at a single hydrostatic pressure, the relative vapor pressures must be reduced to the same hydrostatic pressure.

The change in hydrostatic pressure on swelling is given by

$$\Delta P = k\frac{\Delta V}{V},$$

where ΔV is the swelling from zero moisture content, V is the volume of the fibers at zero moisture content, and k is the bulk modulus. k can be written in terms of Young's modulus, E, and the Poisson ratio, σ, which gives

$$\Delta P = \frac{E}{3(1-2\sigma)} \cdot \frac{\Delta V}{V} = \frac{E}{(1-2\sigma)} \cdot \frac{\Delta r}{r},$$

where r is the radius of the fiber and Δr is the change

in radius on swelling. $\Delta r/r$ can be obtained from a microscopic examination during swelling. Poisson's ratio and Young's modulus are not generally known. For wool, Cassie used a Poisson's ratio of 0.25, which is a common value for solids and not far from that of horn keratin, which has a molecular structure similar to that of wool and a Poisson ratio of 0.35. The Young's modulus was determined from the stress-strain curves of wool at various humidities made by Speakman [54]. The assumption must also be made that the wool fibers are isotropic with respect to elastic properties.

Once the change in hydrostatic pressure is known, the vapor pressures can be reduced to a common hydrostatic pressure through the equation

$$\Delta P = \frac{RT}{M_v} \ln \frac{h_0}{h},$$

where h_0 is the observed vapor pressure, h is the vapor pressure at the standard hydrostatic pressure (in this case, the value at zero regain), and M_v is the molar volume of the adsorbed liquid. The isotherm obtained by plotting the regain against the reduced vapor pressures is no longer sigmoid. A test of Cassie's equation on the reduced isotherm indicates good agreement.

It is also possible to introduce the free energy term for the swelling of the gel directly by making assumptions as to the nature of the gel network and the gel vapor interaction. The nature of the assumptions necessary is determined by consideration of the phenomena associated with the gel vapor interaction as given in part I of this paper and by data on the nature of the gel structure from x-ray and other techniques. In other words, rather than deal with the macroscopic moduli, it is possible to deal with the molecular properties of the gel.

The direct introduction of the molecular swelling properties of the gel network was first done by Flory and Rehner [25] for the case of rubber. This treatment applies to cases in which the main term in the free energy of mixing of gel and liquid is an entropy term and the heat effects are small. In other words, no sites of high reactivity are present in the gel. This is particularly true of the case of rubber in nonpolar liquids such as benzene. At equilibrium the free energy change on mixing is equal to the free energy change of swelling for the network.

The entropy of mixing of long-chain molecules with small molecules has been developed by Flory [24] and Huggins [36]. The entropy, given in Flory's notation, is

$$\Delta S_D = -k\left[n \ln\left(\frac{n}{n+Z\nu}\right) + \nu \ln\left(\frac{Z\nu}{n+Z\nu}\right)\right],$$

where k is the gas constant per molecule, n is the number of small molecules per unit volume, ν is the number of chains per unit volume, and Z is the number of segments, equal in volume to an adsorbate molecule, per chain. The entropy change for isotropic swelling of a polymer network is given by

$$\Delta S_S = -k\nu[\ln \delta^3 + \tfrac{3}{2}(\delta^2 - 1)],$$

where δ is the degree of swelling and is given by $(V'/V)^{\frac{1}{3}}$, where V is the unswollen network volume and V' is that of the swollen network. The derivation of this equation and the postulates from which it is derived will be discussed in section IIB. Dilution of the polymer network will cause an increase in entropy, and swelling will cause a decrease in entropy. Since $Z\nu/(n + Z\nu) = V/V'$, the total entropy change of the mixing process is

$$\Delta S = -kn \ln\left[\frac{n}{n+Z\nu}\right] - \tfrac{3}{2}k\nu\left[\left(\frac{n+Z\nu}{Z\nu}\right)^{\frac{2}{3}} - 1\right].$$

The partial molal entropy change of the adsorbate molecules compared to the liquid state is, by partial differentiation with respect to n,

$$\Delta \bar{S}_1 = -R[\ln(1 - v_2) + v_2] - \left(\frac{R}{Z}\right) v_2^{\frac{1}{3}},$$

where v_2 is the volume fraction of polymer given by $Z\nu/(n + Z\nu)$.

At equilibrium the partial molal free energy of the adsorbate in the vapor and adsorbed states is identical. Assuming negligible heat of swelling,

$$\Delta \bar{F}_2 = -T\Delta \bar{S}_1 = RT\left[\ln(1 - v_2) + v_2 + \frac{R}{Z} v_2^{\frac{1}{3}}\right]$$

for the adsorbed molecules. For the vapor

$$\Delta \bar{F}_1 = RT \ln a_1 = RT \ln \frac{P}{P_0}$$

if the vapor is assumed to be an ideal gas. These two equations give the adsorption isotherm since the regain occurs as the variable in v_2.

A small heat term of the van Laar type can be introduced into the free energy expression but it must necessarily be small enough that the entropy of mixing is not altered. This is acceptable in the case of rubber in nonpolar solvents. However, for

water on textile fibers and other polar materials the heat and entropy of swelling at low and moderate regains indicate that this assumption cannot be made. Hence this theory cannot be used in these cases.

B. Development of Isotherm Used in This Paper

It is probable that the two different general methods of treating adsorption which were mentioned in the previous section—namely, surface adsorption and solution adsorption—are not so different as they may appear. Hill [35] has derived the Brunauer-Emmett-Teller isotherm, originally derived kinetically [10], by the methods of statistical mechanics. To do this, the existence of a certain number of sites of strong bonding must be postulated. However, it need not be postulated that these sites represent a primary surface layer. They might equally well be distributed throughout a volume provided that all were equally accessible. The method of determining the available configurations of the weakly adsorbed molecules merely demands that entropy of mixing terms, such as were discussed in the previous section, do not exist. Hence the equations for multilayer surface adsorption and for extremely imperfect solutions in which mixing terms are negligible have the same form.

An equation will now be derived for an adsorption isotherm in which the free energy changes caused by the swelling of the adsorbent network are considered. The method used follows that used by Hill in deriving the Brunauer-Emmett-Teller isotherm.

It is assumed that there are a certain number of sites per gram of adsorbent on which liquid molecules can form stronger bonds than is possible in the liquid state. In addition, other adsorbate molecules, which are assumed to be in a state thermodynamically identical with the liquid adsorbate, can be adsorbed. The adsorbent is assumed to be a completely nonporous swelling material so that every adsorbate molecule contributes its molecular volume to swelling the adsorbent.

The subscript *1* will be used to denote the adsorbate and the subscript *2* to denote the adsorbent where necessary for clarity. The subscript *s* will be used to denote adsorbate molecules on the sites of strong bonding; the subscript *L*, the rest of the adsorbate molecules.

The partition function for an adsorbate molecule of the *s* type can be written

$$q_s = \left(\frac{kT}{h\nu_s}\right)^3 je^{E_s/kT} = j_s e^{E_s/kT},$$

where j is the partition function for the internal degrees of freedom of the adsorbate molecule, ν_s is the characteristic vibration frequency of the strongly adsorbed state, $-E_s$ is the energy which characterizes the s state, k is the gas constant, h is Planck's constant, and T is the absolute temperature.

The partition function for an L-type molecule can be written

$$q_L = \left(\frac{kT}{h\nu_L}\right)^3 je^{E_L/kT} = j_L e^{E_L/kT},$$

where ν_L is the characteristic vibration frequency for the liquid state, $-E_L$ is the energy characterizing the liquid state, and the other symbols are as given above.

Let there be B localized sites per gram of adsorbent; let α molecules be adsorbed, x of them on localized sites at a given relative vapor pressure P/P_0. The partition function for the molecules on the localized sites is then

$$Q_s = \frac{B!}{(B-x)!x!}\left[j_s e^{E_s/kT}\right]^x.$$

The partition function for the L-type molecules is

$$Q_L = \frac{(\alpha-1)!}{(\alpha-x)!(x-1)!}\left[j_L e^{E_L/kT}\right]^{\alpha-x}.$$

The ratio of factorials represents the number of ways $\alpha - x$ identical molecules can be put on top of x molecules with no restrictions on how many fall on top of a given x molecule. Let Q_N represent the partition function for the swollen adsorbent network without further specifying its form, temporarily, except to state that it is dependent on α but independent of x by assumption. The complete partition function for the system is then:

$$Q = \sum_{x=1}^{K} Q_s Q_L Q_N$$

$$= Q_N \sum_{x=1}^{k} \frac{\alpha!B!}{(\alpha-x)!(B-x)!(x!)^2} \times (j_s e^{E_s/kT})^x (j_L e^{E_L/kT})^{\alpha-x},$$

where 1 has been neglected compared to x and α, and where

$$K = \alpha \qquad \alpha < B$$
$$K = B \qquad \alpha \geq B$$

The approximation is made that log Q is equal to

the logarithm of the largest term in the sum. The value of x which gives this term is determined by

$$\frac{\partial \ln Q_s Q_L Q_N}{\partial x} = 0,$$

or

$$(\alpha - x)(B - x) = \beta x^2, \qquad (A)$$

where

$$\beta = \frac{j_L}{j_s} e^{(E_L - E_s)/kT}.$$

The partial molal free energy of the water is given by

$$\frac{\mu_1}{kT} = -\frac{\partial \ln Q_s Q_L Q_N}{\partial \alpha} = \ln \frac{\alpha - x}{\alpha} - \frac{E_L}{kT} - \ln j_L + \frac{\mu_{N1}}{kT},$$

where μ_{N1} is the partial molal free energy change of the adsorbate from the swelling of the adsorbent network from the perfectly dry standard state.

For the vapor phase

$$\frac{\mu_{V1}}{kT} = \frac{\alpha'}{kT} + \ln P,$$

where μ_{V1} is the partial molal free energy change of the adsorbate vapor, α' is a constant, and P is the vapor pressure.

At equilibrium

$$\ln \frac{\alpha - x}{\alpha} - \frac{E_L}{kT} - \ln j_L + \frac{\mu_{N1}}{kT} = \frac{\alpha'}{kT} + \ln P;$$

for the pure liquid adsorbate

$$-\frac{E_L}{kT} - \ln j_L = \frac{\alpha'}{kT} + \ln P_0.$$

Hence by subtraction

$$\ln \frac{\alpha - x}{\alpha} + \frac{\mu_{N1}}{kT} = \ln \frac{P}{P_0}. \qquad (B)$$

Equations (A) and (B) form the adsorption isotherm. B, x, and α can now be expressed in grams per gram rather than molecules per gram.

It is now necessary to evaluate μ_{N1}/kT. Doing this requires information or assumptions about the polymer network and its mechanical properties.

As a preliminary crude case, assume the fiber to be made up of rigid balls or rods held together by N springs. The free energy change for giving N springs a proportional elongation δ is $Nk\delta^2$, so that

$$\frac{\mu_{N1}}{kT} = \frac{2Nk\delta}{kT}\frac{\partial \delta}{\partial \alpha} = \gamma \delta \frac{\partial \delta}{\partial \alpha},$$

where γ is a constant. It will be seen that the same result can be obtained in some cases by more detailed considerations of the molecular structure of the gel.

A basis for an approach in the case of rubber-like substances is provided by the work of Wall and others [72; 25, 37, 43, 63] on the stress developed by imposing a given strain. The strain, in the cases just mentioned, is assumed to occur at constant network volume. Halsey and Eyring [30] and Flory and Rehner [25] developed methods applicable to cases in which a volume change occurs. These methods are based on different assumptions and will both be discussed here. For the time being only isotropic swelling will be considered. Flory's method will be considered first.

The model used is that of a three-dimensional network produced by the random introduction of cross-links into a mass of long polymer molecules. The segment of long polymer molecules falling between two successive cross-links is referred to as a chain. A cell is then defined as consisting of a cross-link and its four nearest neighbor cross-links. By nearest neighbor cross-link is meant a cross-link occurring at the other end of one of the chains joined by the central cross-link. It does not refer to a spatially close but remotely connected link.

It is then assumed that the actual network can be replaced by an ideal network in which all of the chains are of the same contour length. The distribution of displacements, which are the vectors between the ends of the chains, is assumed to be given by [42]

$$n(xyz)dxdydz = \frac{N\beta^3}{\pi^{\frac{3}{2}}} \exp\left[-\beta^2(x^2+y^2+z^2)\right]dxdydz,$$

where $n(x, y, z)$ is the number of displacement vectors which have coordinates between x and $x + dx$, y and $y + dy$, and z and $z + dz$. β for a flexible chain of Z bonds with a length l between bonds is given by [22]

$$\beta^2 = \tfrac{3}{4}Zl^2.$$

It is then assumed that the most probable positions for the nearest neighbor cross-links to a given cross-link are the corners of a regular tetrahedron the dimensions of which are determined by the constant in the displacement distribution function. Finally it is assumed that the restraints put on a given cross-link in the actual network can be replaced by the restraints imposed by keeping the

nearest neighbor cross-links at the corners of the regular tetrahedron, and that the properties of the given network in deformation can be computed from the properties of the idealized cell.

The number of highly deformed unit cells will be small because of entropy factors imposed by the displacement distribution function so that the network will conform most closely to the properties of the average cell.

The construction of the network is considered to be divided into three steps: (1) addition of $\nu/4$ cross-bonds to ν chains to form $\nu/4$ nuclei, (2) addition of $\nu/4$ cross-bonds to the $\nu/4$ nuclei to form the final network, (3) polymerization of the chains to form the original long molecules. The free energy change for formation of the network from long molecules will then be

$$\Delta F_1 + \Delta F_2 - \Delta F_3,$$

where the subscripts refer to the three steps given above.

The probability factors of the individual steps will now be considered. For step (1), three chains are constrained to have ends in the volume element $\Delta\tau$ around an end of the fourth. The exact size of $\Delta\tau$ is determined by chemical considerations such as bond lengths, etc. The probability for step (1) is then

$$\left[\nu!\,\frac{2^\nu}{(4!)^{\nu/4}}\right]\left(\frac{\Delta\tau}{V}\right)^{3\nu/4},$$

where V is the total volume of the network. The factor 2^ν is introduced because of the identity of the chain ends; the factor $(4!)^{\nu/4}$ from the degeneracy of arrangement about the central cross-bond. In addition the $\nu/4$ cross-links must be arranged in the vicinity of the lattice points at the corners of the cells in the final network. This introduces another volume $\Delta\tau'$ and a probability factor $(\Delta\tau'/V)^{\nu/4}$. The symmetry factor for each tetrahedron introduces a further term $(12)^{\nu/4}$. This gives a total probability of

$$W_1 = \nu!\left(\frac{2\Delta\tau}{V}\right)^{3\nu/4}\left(\frac{\Delta\tau'}{V}\right)^{\nu 4}.$$

Using Stirling's approximation, the entropy of step (1) is given by

$$\Delta S_1 = k \ln W_1 = k\nu\left[\ln\left(\frac{\nu}{V}\right) - 1 + \tfrac{3}{4}\ln(2\Delta\tau) + \tfrac{1}{4}\ln\Delta\tau'\right].$$

Considering now step (2), the four chains from the corners must fall within a volume element $\Delta\tau = dxdydz$ within the tetrahedron. The probability for this is

$$\Omega(xyz)(dxdydz)^4 = \prod_{i=1}^{4} W(x_iy_iz_i)(dx_idy_idz_i),$$

where $x_iy_iz_i$ are the coordinates of the volume element referred to the ith corner of the tetrahedron and $W(x_iy_iz_i)dx_idy_idz_i$ is the probability that the ith chain lie in the volume element $\Delta\tau$. For the Kuhn distribution this is $\frac{n(x_iy_iz_i)}{N}\,dx_idy_idz_i$.

$$\Omega(xyz) = \frac{\beta^{12}}{\pi^6}\exp\left[-\beta^2\sum_{i=1}^{4} r_i^2\right].$$

Consider now a set of coordinates with the origin at the center of the tetrahedron, the x axis through an apex of the tetrahedron, and the y axis perpendicular to one of the sides. Let the coordinates of the volume element $\Delta\tau$ be xyz with respect to these coordinates, and let λ equal the distance from the origin to a corner of the tetrahedron. It is proved geometrically that

$$\sum_{i=1}^{4} r_i^2 = 4(s^2 + \lambda^2),$$

where $s^2 = x^2 + y^2 + z^2$.

It is now necessary to integrate over one of the volume elements to give the total probability that the chains meet in a volume element $\Delta\tau$.

$$\begin{aligned}\Omega_0(\Delta\tau)^3 &= \left[\int_\tau \Omega(xyz)d\tau\right](\Delta\tau)^3 \\ &= \frac{4\beta^{12}}{\pi^5}\left\{\int_0^\infty \exp\left[-4\beta^2(\lambda^2+s^2)\right]s^2ds\right\}(\Delta\tau)^3 \\ &= \frac{\beta^9}{8\pi^{9/2}}\exp\left(-4\beta^2\lambda^2\right)(\Delta\tau)^3.\end{aligned}$$

Then for $\nu/4$ tetrahedra

$$\Delta S_2 = \frac{k\nu}{4}\left[3\ln\left(\frac{\beta^3}{2\pi^{\frac{3}{2}}}\right) - 4\beta^2\lambda^2 + 3\ln\Delta\tau\right].$$

For the final step, the formation of long molecules from the chains with many chains per molecule,

$$W_3 \cong \left(\frac{\Delta\tau''}{V}\right)^\nu 2^\nu\nu!,$$

where $\Delta\tau''$ is again a volume element whose size is determined by bond radii.

$$\Delta S_3 \cong k\nu \left[\ln \left(\frac{2\nu}{V} \right) + \ln \Delta\tau'' - 1 \right].$$

The entropy of formation of the network from long molecules in a volume V is given by

$$\Delta S_V = \Delta S_1 + \Delta S_2 - \Delta S_3$$
$$= k\nu \left[\tfrac{3}{4} \ln \left(\frac{\beta^3}{\pi^{\frac{3}{2}}} \right) - \beta^2\lambda^2 + \tfrac{3}{2} \ln \Delta\tau + \tfrac{1}{4} \ln \Delta\tau' - \ln \Delta\tau'' - \ln 2 \right].$$

Consider now an isotropically swollen network and, neglecting the entropy terms of the swelling molecules, consider only the entropy for the swollen network. The same steps may be considered again. The expression for $\Delta S_1'$ is the same as for ΔS_1, except that V is replaced by V', the volume of the swollen network. The same applies to step (2) except that λ is replaced by λ', for the swollen tetrahedron. Step (3) is considered to occur before the chains are diluted and hence to be the same in each case. The entropy of formation of the swollen network from long chains is then

$$\Delta S_V' = k\nu \left[\tfrac{3}{4} \ln \left(\frac{\beta^3}{\pi^{\frac{3}{2}}} \right) - \beta^2\lambda'^2 + \tfrac{3}{2} \ln \Delta\tau + \tfrac{1}{4} \ln \Delta\tau' - \ln \Delta\tau'' - \ln 2 + \ln \frac{V}{V'} \right].$$

The entropy of swelling of the unswollen network is then

$$\Delta S_V' - \Delta S_V = k\nu \left[\ln \frac{V}{V'} - \beta^2\lambda'^2 + \beta^2\lambda^2 \right].$$

Using the Kuhn distribution, $\lambda^2 = \bar{r}^2 = \frac{3}{2}\beta^2$, and

$$\frac{\lambda'}{\lambda} = \delta = \left(\frac{V'}{V} \right)^{\frac{1}{3}} = \frac{1}{v_2^{\frac{1}{3}}},$$

where δ is the degree of swelling and v_2 is the volume fraction of polymer. If heat terms are considered negligible,

$$\Delta F = \Delta A = -T\Delta S = kT\nu[\ln \delta^3 - \tfrac{3}{2}(1 - \delta^2)]$$

gives the free energy change due strictly to swelling of the network where the $P\Delta V$ term in ΔF is neglected as small.

The free energy change for the same case will now be derived by the method of Halsey and Eyring [30]. The assumption is made, in this case, that the chains are effectively independent units, the lengths of which are determined by a distribution function such that $n(xyz)dxdydz$ is the number of chains whose displacement vectors end in the volume element x to $x + dx$, y to $y + dy$, and z to $z + dz$, and $n'(x'y'z')dx'dy'dz'$ is the number ending in x' to $x' + dx'$, y' to $y' + dy'$, and z' to $z' + dz'$. The assumption is now made that all the chains having a given displacement vector are transformed by the applied deformation in the same way. For example, let the deformation be such that the chains whose displacement vectors ended in x to $x + dx$, y to $y + dy$, z to $z + dz$ now have displacement vectors ending in the region x' to $x' + dx'$, y' to $y' + dy'$, and z' to $z' + dz'$. The number of displacement vectors originally in this region is $n'(x'y'z')dx'dy'dz'$. Neglecting $P\Delta V$ changes, the free energy change for these molecules is given by

$$\Delta F_n = \Delta A_n = -kT \left\{ n(xyz)dxdydz \times \ln \left[\frac{n'(x'y'z')dx'dy'dz'}{n(xyz)dxdydz} \right] \right\}.$$

The total free energy change for the deformation is given by summing over the initial distribution.

$$\Delta F = \Delta A = -kT \int\int\int n(xyz) \times \ln \left[\frac{n'(x'y'z')dx'dy'dz'}{n(xyz)dxdydz} \right] dxdydz.$$

It is now necessary to assume some value for the distribution function and the relationship between x and x', y and y', and z and z'. In the case under consideration at the moment Kuhn's distribution will be assumed and the proportional dimensional changes of the displacement vectors will be assumed to be the same as those for the macroscopic dimensions. In other words, $x' = \delta x$, $y' = \delta y$, and $z' = \delta z$ for isotropic swelling where $\delta = (V'/V)^{\frac{1}{3}}$. It should also be noted that $dx' = \delta dx$, $dy' = \delta dy$, and $dz' = \delta dz$. The number in the volume element x to $x + dx$, y to $y + dy$, and z to $z + dz$ is

$$n(xyz)dxdydz = \nu \frac{\beta^3}{\pi^{\frac{3}{2}}} e^{-\beta^2(x^2+y^2+z^2)}dxdydz,$$

where $\beta^3/\pi^{\frac{3}{2}}$ is the normalization factor.

The free energy change on swelling is given by

$$\Delta F = \Delta A = -kT\nu \frac{\beta^3}{\pi^{\frac{3}{2}}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta^2(x^2+y^2+z^2)} \times [\beta^2(x^2 + y^2 + z^2)(1 - \delta^2) + \ln \delta^3]dxdydz$$
$$= -kT\nu[\tfrac{3}{2}(1 - \delta^2) + \ln \delta^3].$$

On comparing this with Flory's value an apparent discrepancy arises since the signs are different for

the second term in the two cases. This is caused by the different approaches used in the two cases.

It will be noted that Flory, by using the same equation for step (3) for the unswollen and swollen networks, has not accounted for the free energy of dilution of the chains. This term is introduced as one of the mixing terms. In the present case the free energy of dilution of the chains has not been introduced with the free energy change of the adsorbate molecules and hence must be added. It is clearly a negative free energy term and has the form, at constant temperature,

$$\Delta A = \int_1^2 P dV = - NkT \ln \frac{V'}{V} = - NkT \ln \delta^3.$$

The total free energy change for the polymer network is then

$$\Delta A = - kT\nu_2^{\frac{3}{2}}(1 - \delta^2).$$

In the Halsey-Eyring case the dilution factor has already been introduced by the expansion of the volume element *dxdydz*. However, the chains are considered as essentially independent units which are transformed, in this case, according to the macroscopic deformation. The fact that, in the case of cross-linking, the ends of the chains are always constrained to a given volume $\Delta\tau$ by chemical forces regardless of swelling has not been considered. The probability that the end of one molecule, in a total volume V, lies within a volume element $d\tau$ of the end of another is $d\tau/V$, or for ν chains it is $(d\tau/V)^\nu$. For the swollen state the volume is V' and the probability factor $(d\tau/V')^\nu$. The change from the unswollen to the swollen state then introduces a free energy factor

$$\Delta A = - kT\nu \ln \frac{V}{V'} = kT\nu \ln \delta^3,$$

so that the total free energy change for the network for swelling is again

$$\Delta A = - kT\nu_2^{\frac{3}{2}}(1 - \delta^2).$$

Introducing this factor in the Halsey-Eyring case is equivalent to assuming that although the chains are long enough to obey the Kuhn distribution function with reasonable accuracy they are still part of longer molecular units, one molecule containing many chains (since end-effects are neglected). This is a common assumption for high polymeric networks arising from the physical picture of network structure. There may be other entropy terms to be introduced depending on the molecular structure of the gel. These will presumably be small.

The use of one distribution function and hence one value of β implicitly assumes that the actual network can be replaced by one in which all the chains have the same length.

Since $\mu_{N1} = \partial\Delta A/\partial\alpha$ it is necessary to express δ as a function of α. The volume fraction of polymer may be written $1/v_2 = (\alpha + Z\nu)/Z\nu$, and since $\delta = (V'/V)^{\frac{1}{3}} = (1/v_2)^{\frac{1}{3}}$,

$$\frac{\mu_{N1}}{kT} = \frac{1}{Z} v_2^{\frac{1}{3}}.$$

For the case considered the complete isotherm is given by the equations

$$(\alpha - x)(B - x) = \beta x^2,$$

$$\ln \frac{\alpha - x}{\alpha} + \gamma v_2^{\frac{1}{3}} = \ln P/P_0,$$

$$v_2 = \frac{Z\nu}{\alpha + Z\nu}.$$

Now that a complete isotherm has been derived for a swelling adsorbent it is necessary to re-examine critically the assumptions made in the derivation with the point of applying the isotherm to individual fibrous materials, particularly textile fibers in this case. The materials examined in this paper are all either cellulosic or protein in nature. The various facts of adsorption as outlined in part I are assumed to apply to all the substances examined although some of the data are lacking for jute, silk, and the non-textile proteins.

The presence of sites of high reactivity, and adsorption of additional water as the liquid are indicated by data on sorption thermodynamics and are probably safe assumptions. The assumption that all the water adsorbed contributes equally to swelling is an approximation. The degree of approximation is unknown but small, as discussed in part ID.

The assumptions made in deriving the free energy of expansion of the network are more serious. The equations as written apply to a rubber-like three-dimensional network. It should be noted, however, that if γ/kT be substituted for β^2 in the Kuhn distribution function the form of the result is not altered, this allows consideration of other than entropy springs. Textile fibers are not rubber-like materials. Secondary chemical bonds are present in all cases. In cellulose, sections of regularly ordered molecules in which the sum of the secondary

bonds on an individual molecule is equal in magnitude to a primary bond give the polymer the three-dimensional network character. In the proteins, primary cross-bonds between chains may be present as well, but secondary bonds occur extensively. The presence and importance of secondary bonds can be demonstrated from x-ray photographs. These secondary bonds introduce heat terms which must be considered in calculating the displacement vector distribution. Hence Kuhn's equation can no longer be applied. Furthermore, in fibrous materials the long molecules are oriented in such a way that the displacement vectors lie nearly along the fiber axis. Entering water molecules must, of necessity, assume positions between polymer molecules. The anisotropic distribution of displacement vectors is then reflected by an anisotropic swelling. For cotton or wool the swelling is almost entirely along the fiber diameter. This anisotropy of swelling must be considered in writing the distribution function. It also alters the relationship between the degree of swelling, δ, and the regain, α, since the degree of swelling is different in different directions for anisotropic swelling.

The method developed by Flory depends on the detailed molecular picture of the network in an idealized state as a set of tetrahedral cells. Although certain deformations of the tetrahedra can be considered, this method cannot in general be applied to textile fibers. The method of Halsey and Eyring is more general. The assumption that all the molecules in a given distribution range are transferred by a deformation to the same new distribution range must be made. However, any distribution function may be used and the way in which the vector coordinates are transformed by the deformation and the way in which macroscopic properties are related to microscopic ones may be varied.

In the original paper [30] a general distribution function of the form, in one dimension,

$$\psi_x = \frac{e^{-(px^2+qx)}}{\int_{-\infty}^{\infty} e^{-(px^2+dx)}dx},$$

was considered. A molecular potential of the form $E = \gamma(x - \delta)^2$, where δ is a displacement of the potential minimum from the center of the displacement vector coordinates, is considered along with the entropy distribution function of Kuhn. This is equivalent to assuming that the peak of the displacement distribution will occur at some value δ rather than at zero for the free network.

$$P = \beta^2 + \frac{\gamma}{kT}, \qquad q = \frac{2\delta\gamma}{kT}.$$

Changes from $n(xyz)$ to $n'(x'y'z')$ which occur either so as to minimize the free energy change for the deformation or so that the microscopic deformation equals the macroscopic are considered. In addition, the possibilities of summing the vectors directly to give macroscopic dimensions or of summing the absolute values are discussed. Using this method, a crude attempt to introduce anisotropy of swelling has been made.

Since a fiber swells about 15 percent in diameter to 1 percent in length at its swelling maximum in water, the approximation was made that a two-dimensional potential could be used for the swelling. The general potential function was used—namely,

$$\psi = \frac{e^{-[p(x^2+y^2)+q(x+y)]}}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-[p(x^2+y^2)+q(x+y)]}dxdy}.$$

The displacement vectors were assumed to change in the same way as the macroscopic dimensions of the fiber, and a correction term was added for the fact that the chains are sections of long molecules. Either method of summing gave the same functional dependence on δ for the partial molal free energy of swelling,

$$\frac{\mu_{N1}}{kT} = \gamma(\delta - 1)\frac{\partial\delta}{\partial\alpha}.$$

In the case of vectorial addition,

$$\gamma = 2\nu(1 + 2y_0^2P),$$

where y_0 is the average contribution of a molecule to the y dimension of a fiber ($y_0 = z_0$, since the two dimensions are considered to be the same).

For addition of the absolute values of the displacement vectors,

$$\gamma = 2\nu\left(1 + \frac{q^2}{2P}\right).$$

Since swelling occurs in only two dimensions,

$$\delta^2 = \frac{V'}{V} = \frac{\alpha + Z\nu}{Z\nu}; \qquad \frac{\partial\delta}{\partial\alpha} = \frac{1}{2Z\nu}v_2^{\frac{1}{2}}.$$

Substituting,

$$\frac{\mu_{N1}}{kT} = \gamma(1 - v_2^{\frac{1}{2}}).$$

In Figures 1 and 2 are shown isotherms using

$$\frac{\mu_{N1}}{kT} = \gamma v_2^{\frac{1}{3}} \quad \text{and} \quad \frac{\mu_{N1}}{kT} = \gamma(1 - v_2^{\frac{1}{3}}).$$

The two isotherms fit the experimental data about equally well and hence it is not possible to choose between the two free energy terms for swelling. The constants used for each theoretical isotherm are given in Table II and it can be noted that B and β are not radically different in the two cases. The values of γ are too large to be $1/Z$ values for rubber-like molecules since Kuhn's distribution would not hold for such short chains. The models correspond to crude approximations to the gel structure in terms of springs.

Certain knowledge of B and β would enable the swelling free energy term to be determined experimentally and permit differentiation between the two forms. These values of B and β are not yet known, however. The theoretical curves are obtained by fitting the equation to the experimental data at three points. This, and considerations of hysteresis effects which will be discussed in the following section, make it impossible to choose a reliable value of B and β. A formal method for determining swelling free energy changes is available in the work of Halsey and Eyring. But until more is known about the distribution functions for displacement length and the laws of mechanical deformation for the general anisotropic case, a satisfactory swelling free energy term cannot be determined independently. Since it is impossible at the present time to choose a satisfactory μ_{N1}/kT on theoretical grounds or to establish one from the experimental data, $\mu_{N1}/kT = \gamma v_2^{\frac{1}{3}}$ was used in general as a simple, more or less empirical term in testing the isotherm on various fibers.

One additional complication may occur especially in the case of cellulosic materials. For cotton, the characteristic spacings taken from the x-ray diagram do not change as water is adsorbed by the fiber, nor are large differences in the intensity of the arcs noted. This indicates that the regions which give the crystalline x-ray diagram are not altered by the adsorption of water. Apparently these regions are accessible to water, however, since in exchange reactions with heavy water a complete exchange of the hydroxyl hydrogens of the cellulose occurs [13].* Apparently water molecules can penetrate into but cannot permanently deform the more ordered regions of the cellulose modification found in cotton. The same was thought to be true for the cellulose modification found in mercerized and regenerated cellulose. However, Hermans [32, p. 42] claims to have observed swelling of the so-called crystalline regions in x-ray diagrams of regenerated cellulose. This swelling depends on the regain. In any case, if the highly ordered regions are not altered upon adsorption, only the unordered regions are being swollen. Hence the volume fraction of polymer used to calculate the free energy change of swelling should not contain the total volume of the polymer but only the volume of the deformed fraction. The corrected volume fraction is then given by

$$v_2 = \frac{(1 - k)\sigma_2}{\alpha\sigma_1 + (1 - k)\sigma_2},$$

where k is the degree of crystallinity, σ_1 is the specific volume of the adsorbate, and σ_2 is the specific volume of the adsorbent.

The "degree of crystallinity" is a poorly defined concept. Originally it denoted that portion of a fiber which contributed to the crystalline pattern in an x-ray fiber diagram. As used above it means that portion of the fiber which is not swollen by water. Technical limitations make it impossible to obtain a quantitative value from the x-ray data. Moreover, since a rather large ordered segment (in molecular dimensions) is needed to produce a visible x-ray pattern, such a value would be a lower limit. Estimates of the degree of crystallinity have been given by Hermans [32] and Nickerson [49] by different methods. Hermans derives a value of about 60 percent for cotton from sorption considerations (see section IIA). Nickerson derives a value

TABLE II

Substance	B	β	γ
Cotton ads. $\mu_{N1} = \gamma v_2^{\frac{1}{3}}$	0.035	0.06	0.31
Cotton ads. $\mu_{N1} = \gamma(1 - v_2^{\frac{1}{3}})$	.030	.03	.36
Cotton des. $\mu_{N1} = \gamma v_2^{\frac{1}{3}}$	.045	.07	.33
Jute ads.	.065	.11	.39
Jute des.	.072	.10	.39
Wool ads.	.090	.105	.345
Wool des.	.100	.08	.37
Silk ads.	.050	.10	.20
Silk des.	.053	.09	.215
Gelatin average	.090	.03	.16
Serum albumin average	.070	.07	.19
Egg albumin average	0.060	0.065	0.16

* Recent work by Mark and Frilette presented at the spring meeting of the American Chemical Society, 1947, at Atlantic City, casts some doubt on this.

TABLE III

Cotton:	Experimental isotherm—Urquhart and Williams [69].
	Specific volume—0.64—Valko [71].
	Degree of crystallinity—0.9—Nickerson [49].
Jute:	Experimental isotherm—Macmillan, Mukherjee, and Sen [45].
	Density—1.559—Macmillan and Sen [46].
	Degree of crystallinity assumed to be the same as for cotton—0.9.
Wool:	Experimental isotherm—Speakman [55].
	Specific volume—0.757—Heertjes [31].
Silk:	Experimental isotherm—Goodings and Turl [29].
	Specific volume—0.714—Heertjes [31].
Gelatin:	Experimental isotherm—Bull [11].
	Specific volume—0.682 (partial specific volume in solution)—Krishnamurti and Svedberg [41].
Serum Albumin:	Experimental isotherm—Bull [11].
	Specific volume—0.748 (partial specific volume in solution)—Svedberg and Pedersen [62].
Egg Albumin:	Experimental isotherm—Bull [11].
	Specific volume—0.749 (from partial specific volume in solution)—Svedberg and Pedersen [62].

of 90 percent from a consideration of the rate of carbon dioxide evolution when cellulose is treated with boiling dilute hydrochloric acid with a catalyst. The method is based on an observed change of rate of evolution which is assumed to occur when the amorphous part of the cellulose is exhausted and the crystalline begins to react. The exact reaction is not known and hence the method is empirically based on the above assumption. Hermans' value depends on the validity of his theory of adsorption. Nickerson's value was used for cotton and it was assumed that it also applies to jute for these calculations. Hermans' value was not known at the time the calculations were made. Since neither method is free from assumptions it is difficult to estimate the relative merit of each. The proteins were assumed to adsorb throughout, in agreement with Heertjes [31] for the fibers and Astbury and Lomax [2] for the other proteins.

Values of the density are needed in determining the volume fraction of the fiber. The variation of density with immersion fluid has already been discussed in part I. However, for the approximate nature of these calculations the differences are small. In the case of some of the proteins, partial specific volumes in solution were used. The value used and the reference are given in Tables II and III for each fiber.

Figures 1–11 show the results of fitting isotherms using the semi-empirical partial molal free energy function (page 544), except for Figure 2.

The constants and data are given in Table III. Some of the specific volumes, and the degree of crystallinity of cotton and jute, are only approximate. The assumption is also probably suspect that the ordered regions of some of the proteins, especially silk, swell.

The constants are gathered for comparison in Table II. The values of B, the number of sites of strong adsorption, vary in the expected way for cotton and jute and wool and silk. The values of β group around 0.07. It is interesting that the value for wool, 0.1, is the same as that found by Cassie [12], who accounted for mechanical effects in a different manner (see section IIA). The mechanical constants split into two groups. With the exception of silk, the fibers are grouped around $\gamma = 0.33$. The reason for silk's apparent difference is not known.

III. Extended Treatment of Adsorption and Swelling

A. Hysteresis and Limited Swelling *

Probably the most stable configuration for a system of long-chain molecules capable of forming strong secondary bonds is a crystal having the parameters which can be obtained from an x-ray fiber diagram. In the actual forming of such a network the length, flexibility, and large number of secondary bonding sites of each chain impose large activation energies and entropies on the formation of a perfect macrocrystal. The resultant network is thus a heterogeneous mixture of regions of vary-

* A somewhat similar discussion of hysteresis was published while this paper was in preparation. *See* Smith, S. E., *J. Am. Chem. Soc.* **69**, 646 (1947).

ing degrees of order. The relative extent of ordered and disordered regions depends on the method of formation. For example, cotton has a greater degree of order than common textile rayon. Once the network is formed, activation free energies for major changes are very large and easily attainable configurations involving minor changes are usually at higher free energy levels. Thus the network exists in a metastable equilibrium. These facts give the networks considered their shape, stability, and rigidity. In wool and probably silk a three-dimensional network of primary chemical bonds is also present, but the influence of the secondary bonds is still great.

Let the interaction of such a network with a polar molecule such as water now be considered. The free energy changes for the idealized reactions

$$H_2O - H_2O + \text{—}\dot{\text{o}}\text{—} \rightarrow H_2O + \overset{H_2O}{\text{—}\dot{\text{o}}\text{—}}$$

and

$$H_2O - H_2O + \overset{\text{—o—}}{\text{—}\dot{\text{o}}\text{—}} \rightarrow 2\ \overset{H_2O}{\text{—}\dot{\text{o}}\text{—}}\ ,$$

where –ȯ– represents a vacant polar bonding site on a residue forming one of the links in a polymeric chain, are not known. For the polymers considered here the free energy change should be negative for the first and probably for the second by analogy with the properties of simple sugars and amino acids. Let it be assumed that the free energy changes for both reactions are negative. In a complex network there are all kinds of such sites, ranging from open ones to ones surrounded in such a way as to produce locally the configuration of the crystalline material. The formation of the activated complex between such a site and water may involve not only the nearest neighbor residues but also other residues further away along the molecular chain. This is the fundamental difference between these residues and their unpolymerized counterparts. Activation of a molecule on the surface of a crystal of sugar can only involve the nearest neighbor molecules. The free energy of activation of a given site is thus a very sensitive and complex function of local and long-range order. Since the long molecular chains are assumed to be at least moderately flexible, a site in a region of low immediate- but high long-range order can still be activated relatively easily. If the free energy of activation is assumed to rise sharply as a function of order, the exponential dependence of the specific rate constant on the activation free energy makes a metastable equilibrium state possible. This is the cause of the related phenomena of limited swelling, adsorption hysteresis, and swelling maxima with temperature.

Suppose such a network to be immersed in liquid water. Water will be adsorbed by the network and swelling will occur. The limitations on the total swelling imposed by the network's mechanical properties have been discussed in section IIB; the factors limiting the magnitude of B are now involved. The sites in regions of low order will be rapidly covered, but as the degree of order increases, exponential dependence of k on $\Delta F^{\ddagger}$ and of th. sensitivity of $\Delta F^{\ddagger}$ to order may cause a rather sharp boundary between sites easily covered and those having an activation free energy so great that for all practical purposes they are unreactive, or, if they do react, are in such a strained position that return to the initial state causes a local decrease in free energy and has a low activation barrier. The distribution of sites among the various possible degrees of order caused by the initial formation of the network can also contribute to the sharpness of this boundary. Lowly populated levels of intermediate order would increase the sharpness of the barrier. It is thus clear that a definite amount of water can be taken up by the network and a state attained in which all small changes are to higher energy levels and all greater changes have very high activation barriers. The effects of temperature variation can now be explained. Increasing the temperature decreases the adsorption, as is to be expected for an exothermic reaction. However, at the highest humidities, when the fiber is highly swollen, the number of B sites can be increased by a process similar to sintering at higher temperatures. The extent to which B can be increased is usually limited so that a maximum occurs. The absence of the maximum at lower relative humidities makes it evident that the mechanical properties of the fiber play an important part and that the fiber must be swollen.

Let a completely dry network now be considered and let the previous history of the network be such that it is in its (metastable) equilibrium configuration at that temperature. This is done to exclude consideration of aerogels temporarily. Let the network now be allowed to come to equilibrium with atmospheres of increasing relative humidity. Water molecules are adsorbed and swelling occurs. This swelling breaks secondary bonds between network

residues, causing the number of B sites to increase. As a relative humidity of 1 is reached the number of B sites is limited, as shown above, and the total adsorption is limited by the number of B sites and the mechanical properties of the network. Desorption is now allowed to occur and the network contracts. If it is assumed that the contractive forces of the network are unable to push off molecules adsorbed on B sites, there is a larger B value on desorption than there was at the same partial vapor pressure for adsorption and hence there will be a higher regain.

Actually, the water molecules are in a dynamic equilibrium and any one site may be vacant at any time. However, the fraction of any time interval during which it is vacant is small at first and increases as the relative humidity decreases. Let the following idealized case be considered. Two neighboring chains have four corresponding sites of attraction at which they can form bonds either with each other or with water (see Figure 12). Let the sites be covered with water. The expanded network exerts a force to close the hole which is not great enough to remove the water. The assumption is made that the chains are stiff enough to require that all four sites be freed at the same time for strong bonds to be made with the other chains. At relatively high partial vapor pressures the chance that all sites will be vacant simultaneously is small. As the partial vapor pressure outside decreases, the fraction of time each site is vacant increases and the chance of closure increases. Thus sorption hysteresis is a mechanical lag in the response of the network structure caused by the strong adsorption of molecules on geometrically important sites. The allied phenomena of hysteresis, such as the effects of special pretreatments and attainment of intermediate regions between the standard isotherms, are understandable on the same basis.

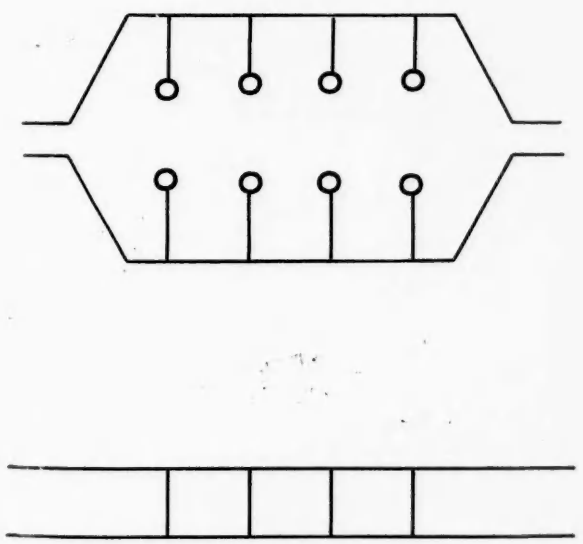

FIG. 12. *Schematic diagram of two adjacent long-chain molecules having polar groups with and without complete adsorption of water.*

It is not claimed that the above explanation of hysteresis is different in content from that of Urquhart [66] but rather that it is a clarification and rewording in terms of the theory of absolute reaction rates [28] and the recent advances in understanding the network structure to disclose the theoretical basis for Urquhart's work.

The results of the application of the theory of adsorption outlined in this paper are in semi-quantitative agreement with the above picture of the causes of adsorption hysteresis. Examination of the constants for adsorption and desorption for the same sample discloses that B increases on going from adsorption to desorption, β increases slightly for cotton but decreases for the other materials, and changes in γ are all under 10 percent. When the sensitivity of the isotherm to changes in the constants is considered, the relative change in B is magnified. The changes in γ and β lie close to the limits of accuracy in fitting the curve. By this is meant the limits of the mechanical fitting, not the theoretical limits of the equation. Hence it can be said that the number of sites per gram for strong adsorption increases on going from the adsorption to the desorption curve at a given relative humidity, while the free energy change for adsorption on these fixed sites and the larger structural features which determine the mechanical properties of the network remain unchanged. The small change of B for silk, reflecting the small sorption hysteresis compared to that of cotton or wool, emphasizes again the fact that silk is different in behavior from the others. Apparently it is similar to the nonfibrous proteins except for the presence of fewer B sites.

It is interesting to note that nylon, which is formed of long hydrocarbon-like chains with polar groups on the ends (many chains per molecule making a roughly periodic structure), could not be expected to have the complex network behavior necessary for much hysteresis. This offers a possible explanation for the lack of hysteresis observed by Speakman and Saville [58].

changed. Instead of this, the change is observed to be a gradual one, the 101 plane separation changing gradually with moisture regain. The problem of crystalline patterns which swell in this way is hence still incompletely understood. In addition to rayon, gelatin and the other proteins and probably silk and wool are in this class.

It is of interest to compare the values of B obtained from isotherms with the total number of possible hydrogen bond sites in a gram of polymer. For cotton, the residue mole weight is 162. There are thus $N/162$ possible hydrogen bonding sites in a gram of cotton, assuming that there is one site per residue. $BN/18$ is the number of sites used for water adsorption. The ratio of the two values shows that 32 percent and 41 percent of the possible sites in the amorphous portion of the cellulose are used for water bonding on adsorption and desorption, respectively. If it is assumed that there are three sites per residue these values are 11 percent and 14 percent, respectively. Apparently there is enough contact between chains, even in the amorphous region, so that a large number of the possible sites are satisfied within the network structure and are unavailable for bonding water.

Pauling [51] has considered the isotherms of the proteins and values of B obtained from a direct application of the two-constant Brunauer-Emmett-Teller equation to the lower-regain region of the isotherm given by Bull [11]. The polar side-chains of the amino acids are considered to be stronger bonding sites than the C=ONH groups along the protein chain. Using the values 228 moles/105 g. for silk and 341 moles/105 g. for the number of polar groups per unit weight and Bull's values of B, it is found that roughly all of these polar groups are covered. Using Pauling's values for the number of polar groups per unit weight and the B values obtained in this paper, the values are 125 percent for silk and 155 percent for wool. This means that there are more strong bonding sites than those provided by polar side-chains.

The mean residue of silk fibroin has been given by Bergmann and Niemann [8] as 84. According to Cohn and Edsall [15], the four major constituents of wool keratin are leucine 11.5 percent, arginine 10.2 percent, glutannic acid 15.3 percent, and aspartic acid 7.3 percent. All other constituents are below 5 percent; the total, 71.4 percent, indicates that there are other constituents and that some of these percentages are incorrect, since complete analysis corresponds to about 110 percent (the amino acids are considered as such, not as residues). By assuming that wool is made up entirely of these four constituents, or, in other words, that the rest of the constituents will not change the mean residue weight, a mean residue weight of about 126 is obtained as a very rough value. Assuming all polar side-chain sites to be covered, 5 percent in the case of silk and 24 percent in the case of wool of the peptide linkages are sites for the adsorption of water. Again, presumably a large fraction of the possible bonding sites are used to hold the protein structure together.

β is a ratio of the partition functions of water in the liquid and firmly adsorbed states and as such is a measure of the free energy change when liquid water is adsorbed. The value of β depends on the definition of B. If it is assumed that the actual distribution of sites of varying bonding strengths can be replaced by a number, B, of sites having the bonding strength of an open polar group, β can be estimated if experimental thermodynamic data in the low-regain region are known.

$$\Delta F^0 = \Delta H^0 - T\Delta S^0 = -RT \ln \frac{Q_S}{Q_L} = RT \ln \beta.$$

For cellulose, $T\Delta S \cong 80$ cal./g. and $\Delta H \cong 230$ cal./g. at zero regain [71]. At 300°K, these values give $\beta \cong 0.01$. The values from the experimental isotherms are $\beta \cong 0.06$. Cassie [12] obtains the same order of magnitude from estimating the frequencies in the classical liquid partition function used and using experimental heats of swelling.

It is useless to speculate on methods of evaluating γ independently until a sounder theoretical basis for the form of the network swelling term is provided. However, evaluating B and β from low-regain data, where the contribution of this term to the partial molal free energy of the water is small, and the subsequent evaluation of this contribution at other regains experimentally, affords a method of studying this term directly. This would be particularly interesting in the case of fibers of different degrees of orientation or of different degrees of crystallinity such as have been produced by Hermans [32].

The determination of γ from the mechanical properties of the fiber is not possible until more is understood about the distribution functions for vector displacements and the effects of orientation on mechanical properties.

The number of sites per gram, B, is thus not a constant but a function of the regain α. The values of B obtained from fitting the curves are thus average values. That such values can be used at all can be explained as follows: The value of B probably changes most rapidly in the region of greatest swelling which occurs at the higher relative humidities (>0.7). In this region the isotherm rises steeply, almost parallel to the regain axis, and small errors in the constants used for fitting are not so noticeable. On desorption the reverse is probably true and the return to the original network structure occurs for the most part in the sharply rising region of initial regain at low relative humidities. That such a return to initial configuration does occur is shown by the reproducibility of the sorption cycle on recycling (see section IB).

The study of the dependence of B on regain and further experimental proof of this theory of sorption hysteresis involve the study of various cyclic sorption histories. According to these ideas the lowest section (with respect to relative humidity) of the adsorption isotherm should be reversible. Cyclic sorption histories between two given relative humidities should give reproducible isotherms lying within the envelope of the two standard sorption isotherms. The form of B is probably $B = B_0 + f(\alpha_0 - \alpha)$, where only positive values of $\alpha_0 - \alpha$ are considered. The value of B_0 could be determined from that part of the primary adsorption curve which is reversible, if such a region exists. Although the general outline is clear, a quantitative determination of the changes in B must await further clarification of the value of μ_{N1} and a better fitting technique, preferably one using at least one constant determined from an independent source.

B. The Constants of the Isotherm

The relation of the constant, B, to molecular parameters is obscure. An isolated polar group in the network is clearly one of the B sites. But, as polar groups are considered which are increasingly satisfied by other polar groups of the network, the free energy change for adsorption of water molecules on these sites compared to liquid water becomes smaller and smaller. There are two ways of defining B exactly and the definition used influences the value of β. B can be defined as a number of identical sites of a given type (value of β) which will give the same isotherm and thermodynamic effects as the actual distribution. An alternative is to consider all sites on which $E_S \neq E_L$ as B sites. In this case either a distribution function for the B's as a function of the β's must be written or β must be considered to be an average value. The first method makes calculating β from thermodynamic data a possibility, as will be discussed later.

A further complication is introduced by the presence of regions giving selective x-ray diffraction patterns. In the case of cotton these regions apparently are unaffected by the adsorption of water. For rayon, Hermans [32, 34] claims that there is a gradual increase of about 0.5 Å. for the 101 spacing of the cellulose lattice, the other lattice constants being unchanged on passing from 0 to 85 percent relative humidity. Experiments were done to try to show that this transformation was actually caused by the presence of water and not by a transformation in the crystalline phase catalyzed by water but not incorporating water into the structure. The conclusion was reached that the change was brought about by hydrate formation. From density considerations the formula of the hydrate was given as $C_6H_{10}O_5 \cdot \frac{1}{3}H_2O$ or $C_6H_{10}O_5 \cdot \frac{1}{2}H_2O$.

Certain difficulties arise from this explanation. Geometrically it is difficult to understand how a water molecule can be shared by two or three glucose residues so as to increase the 101 spacing by 0.5 Å. The 101 plane contains a number of hydroxyl groups and the spacings might presumably be thought to be determined by the hydrogen bonds between neighboring glucose residues. The introduction of one water molecule between two glucose residues so that no one glucose residue bonded more than one water molecule would correspond to one of Hermans' formulas. This would replace a residue-residue bond with two residue-water bonds. According to Pauling [50], the OHO distance of a hydrogen bond ranges from 2.5–2.9 Å. Insertion of water molecules might then be expected to increase the distance between the 101 planes by nearly this amount. Rotation of residues in the unit cell might make the increase somewhat smaller, but probably not so small as 0.5 Å. unless the other lattice parameters were changed. The bonding of one water molecule with three glucose residues calls for forces different from those in the usual hydrogen bond. In addition, for the formation of a true crystalline hydrate from an anhydrous crystal form it would be expected that the anhydrous pattern lessened in intensity as the intensity of the hydrate pattern increased as the proportions of the two

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The effect of temperature variations on adsorption is another potential source of information on the values of the constants as well as on hysteretic effects. Several interesting effects have been mentioned in part I. Some of these have been explained in the section on hysteresis. The use of isotherms at different temperatures to evaluate constants of the adsorption process, other than the heat of adsorption, has not been done. The isotherms of Wiegerink [73] for purified cotton at 35.5°C, 70°C, 100°C, 125°C, 150°C were fitted with the isotherm developed in this paper, but no conclusions could be drawn about the temperature variation of the constants. This is not unexpected since the complete isotherm is never given. At moderate temperatures the region from 20 percent to 80 percent relative humidity is given. At high temperatures, only that part of the isotherm for which P is less than 1 atmosphere is given. The resulting curves cannot be used to determine critically the three constants of the isotherm.

β is obviously temperature-dependent, B probably increases slightly with increase in temperature, and the temperature effect on γ is unknown.

Acknowledgment

The authors wish to thank Dr. J. H. Dillon for reading and criticizing the manuscript, and Miss Corneil Messler for preparing the illustrations.

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The Partial Carboxymethylation of Cotton to Obtain Swellable Fibers, I

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Abstract

For the purpose of obtaining quickly swellable fibers to aid in making cloth less pervious to water, cotton fibers have been partially carboxymethylated. Different degrees of swelling have been obtained and the properties of the resulting products are described.

A PROMISING approach to the problem of increasing the usefulness of cotton is the chemical modification of the cotton after its manufacture into yarn or cloth, while at the same time preserving its fibrous nature. A notable example is the partial acetylation of cotton [13] to yield a cloth or thread which is very resistant to rotting. The present article decribes a method of improving cotton by partial carboxymethylation and points out some of the desirable properties produced by the treatment. The immediate object was to prepare a highly swellable cotton so that the permeability of the cloth to water would be decreased.

The fabrics known as Shirley cloths are specially woven [20] to make them permeable to air when dry but only slightly permeable to water when damp. This property is due to the decrease of space between the fibers as well as that between the yarns by virtue of the swelling of the fibers and is enhanced by the construction of the fabric. It has long been known that linen fibers swell quickly on exposure to water, and for this reason linen is used for fire hose. The shortage of linen during the war prompted Goldthwait [12] to substitute treated cotton for linen. The cotton was impregnated with the hydroxyethyl ether of cellulose to a take-up of about 6 percent. The ether, although insoluble in water, swelled quickly on exposure to water and made a cotton fire hose watertight. Stallings [25] recently patented the treatment of cellulosic fibers with acrylonitrile in the presence of sodium hydroxide to make leak-resistant, fireproof fire hose. Presumably, such treatment gives a partially substituted carboxyethyl ether of cellulose; a more vigorous treatment gives an alkali-soluble product [5] which does not, however, dissolve in water.

It is well known that the sodium salt of carboxymethylcellulose is completely soluble in water, providing the degree of substitution is approximately 1 carboxymethyl group per 2 glucose units or greater; and it was therefore reasonable to believe that carboxymethylation to an extent less than that which would give solubility would allow swelling which would be more or less proportional to the degree of substitution. This has proved to be true.

The preparation of carboxymethylcellulose using chloroacetic acid and sodium hydroxide was patented in Germany [10] in 1921, and the sodium salt of carboxymethylcellulose has lately been introduced commercially into this country. It is valuable as a thickening agent or for stabilizing emulsions. Its uses and applications have been exhaustively reviewed [16], and its commercial preparation has been described recently [2]. Lilienfeld [17] has patented the treatment of cloth with chloroacetic acid followed by mercerization to obtain a changed finish and novel dyeing effects. Chowdhury [8] has done some work on the carboxymethylation of purified cellulose, particularly to obtain alkali-soluble products.

In the work detailed here, we have investigated those conditions which yield partially carboxymethylated cotton (about 1 carboxyl per 5 to 40 glucose units). In general, cotton was impregnated with the required quantity of monochloroacetic acid and then treated with strong sodium hydroxide for about ½ hour or longer. The process did not degrade the cotton as judged by its tensile strength, or change its hand or appearance greatly from that of ordinary mercerized cotton. Viscosities of the cuprammonium

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solution were not determined because of the formation of a precipitate with the copper. The change in swelling capacity was measured, and the properties of the resulting product were investigated. By replacement of the sodium of the partially carboxymethylated cotton with metals which form insoluble salts, such as copper, mercury, or silver, the resistance of the cotton yarns to microbiological attack was greatly increased.

Cloth in the piece has also been partially carboxymethylated and this treatment yielded rather different properties from those of cloth woven from the treated yarns. The work on cloth will be described in a subsequent communication.

Experimental Procedures

Determination of Degree of Substitution of Carboxymethylcellulose

A number of soluble preparations of carboxymethylcellulose were made, and these, together with a commercial product, were used as a basis for selecting the most convenient method of estimating the degree of substitution. Chowdhury [8] had prepared the copper or silver salt and analyzed it for the metal content. He had also made the free acid, dissolved it in excess standard base, and back-titrated. Eyler, Klug, and Diephus [11] recently described a similar titration and also a method of hydrolysis to yield glycolic acid with subsequent colorimetric determination using 2,7-dihydroxy-naphthalene. Since copper is easily determined either gravimetrically or volumetrically, with a considerable range of application, the method involving the preparation of the copper salt and subsequent determination of the copper was selected by the authors after they had established the validity of the method by the experiments described in the following paragraphs.

The copper, lead, aluminum, mercury, zinc, titanium, iron, chromium, tin, and silver salts of carboxymethylcellulose are reported to be nearly insoluble in water [3, 16, 21]. The present investigation showed that the thorium and uranyl salts are also nearly insoluble. A number of these salts, as well as the free acid, were prepared from a commercial sample of the sodium salt as follows: One hundred grams of the sodium salt were dissolved in 2 liters of water, centrifuged, and filtered through a fritted glass filter to remove insoluble fibers. The solution was found to have a pH of 6.5, indicating that the salt was deficient in sodium; and sodium analyses, as given in Table I, showed this to be so. The pH was raised to 8.1; the sodium salt was precipitated by addition of ethyl alcohol, washed with alcohol, and then used as a stock material to prepare the free acid and salts. The acid was made by dissolving the sodium salt in water and bringing it to a pH of 2.5 with hydrochloric acid, which yielded a gelatinous mass. This was thoroughly beaten in a Waring Blendor, coagulated with ethyl alcohol, decanted, washed with ether, filtered, and dried *in vacuo* at 50°C. The residue was ground to approximately 40-mesh size and extracted with hot water until no chloride could be detected in the washings. It was then dried. The insoluble salts were prepared by the addition of about a 2-percent solution of the sodium salt of carboxymethylcellulose to approximately a 50 percent excess of a 2-percent solution of the precipitating salt. After the beating in the Waring Blendor, the mixture was allowed to stand overnight in order to assure thorough penetration. The precipitate was then filtered, thoroughly washed with water, dried, and the percentage of metal was determined.

TABLE I. METAL SALTS OF CARBOXYMETHYLCELLULOSE

Sample	Precipitating salt	Metal	
		Actual (%)	Theoretical* (%)
Sodium salt	—	8.23, 8.24†	8.24
Lead salt	Lead acetate	29.88, 29.98	28.80
Copper salt	Cupric sulfate	11.10, 10.95	11.04
Copper salt	Cupric acetate	16.18, 16.12	11.04
Aluminum salt	Aluminum sulfate	3.48, 3.46	3.39
Silver salt‡	Silver nitrate	27.18, 27.09	29.64
Titanium salt	Titanium trichloride	11.07, 11.01	5.87
Thorium salt	Thorium nitrate	22.31, 22.41	18.47
Uranyl salt	Uranyl nitrate	31.27, 31.07	30.43

* Theoretical values are based on a neutral equivalent of 257.1 of the acid prepared from the sodium salt or a substitution of 0.813 carboxymethyl groups per glucose unit.

† Percent sodium in commercial salt was 7.22 and 7.15.

‡ The silver salt turned brown very rapidly when exposed to light.

Since direct titration of the acid was slow and tedious because of its relative insolubility, it was dissolved in excess standard potassium hydroxide and back-titrated with standard acid. The neutral point was found to be at pH 8.1 when a potentiometric curve was made using the Buras-Reid titrimeter [7] for the determination. These results substantially agree with those of Brown and Houghton [6]. Shaw [21] has determined the apparent pK (the

negative log of the dissociation constant) to be 3.68. Thymol blue was used satisfactorily as an indicator for some titrations. The neutral equivalent of the acid prepared from the stock material was 257.1, which corresponds to an average of 0.813 groups per glucose unit. The analyses of some of the compounds prepared are summarized in Table I.

It will be observed from Table I that the thorium and titanium salts contain much more metal than the theoretical amount. Possibly this is due to steric hindrance, a phenomenon noted by Speakman and Chamberlain [24] with the aluminum salts of alginic acid in the preparation of alginate fibers. In fact, they found aluminum to act as though its valence were only 1.38. If the carboxymethyl group is attached at the 6-carbon position, there is a great similarity between the product and the pyranose structure of alginic acid [18]. The authors have found that a solution of the sodium salt of carboxymethylcellulose can be readily spun into strong fibers in precipitating baths containing soluble salts of lead, aluminum, copper, or mixtures of such salts. The fact that the aluminum salt shown in Table I contains the theoretical amount of aluminum may be due to the greater availability of the carboxymethyl group. The bivalent metals apparently form salts in which 2 carboxyl groups unite with the metal. This is not surprising since it has been noted by Sookne and Harris [23] that the calcium ion unites quantitatively with the carboxyl group of oxycellulose.

It was realized that the use of a solution of cupric sulfate as the precipitating agent introduced the possibility of error because of competition between acids for the copper, but the use of a weaker acid salt, such as cupric acetate, introduced the possibility of greater error owing to formation of cupric hydroxide or even cuprous oxide. This may explain the large amount of copper obtained in one of the examples in Table I. The possibility of the formation of a double salt with cupric acetate was considered, but analyis for acetyl content gave negative results.

This method of determination using cupric sulfate was of sufficient accuracy for use as a control method to indicate the degree of substitution. The method may be used for either soluble or insoluble materials. The procedure is as follows:

If the compound is soluble, dissolve in water so as to obtain an approximately 2-percent solution and add this to a 50 percent excess of a 2-percent cupric sulfate solution, stirring vigorously, as with a Waring Blendor. Allow to stand overnight, filter, and wash thoroughly with hot water. Dry and determine the copper content by the method of Hoffpauir and O'Connor [15]. If, as with partially carboxymethylated materials, the compound is not soluble, soak in 2-percent cupric sulfate solution overnight, wash thoroughly with hot water, dry, and weigh. Extract the copper from the material by three washings with 5-percent sulfuric acid. Determine the copper content in the solution or from an aliquot as before.

Carboxymethylation of Purified Fibers

The effect of change of time, temperature, and concentration of reagents on the degree of substitution was investigated with the object of determining optimum conditions without formation of a soluble or degraded product. The copper content of the copper salt was used as a criterion of the degree of substitution. A copper content of 7.7 percent corresponds to a substitution of 1 carboxyl group for every 2 glucose residues, and the sodium salt of this compound is soluble. Cellulose with uniform substitution of approximately 1 carboxyl for every 4 glucose residues was gelatinous but not soluble. A typical preparation is as follows:

Five grams of purified cellulose linters were impregnated with an equal weight of a 50-percent solution of chloroacetic acid. The material was partially dried and then treated with 40 grams of 36-percent sodium hydroxide to obtain an approximately 33-percent residual solution of sodium hydroxide. After 1 hour, the product was washed thoroughly with water. Analysis of the copper salt gave 4.51

TABLE II. VARIATION IN DEGREE OF CARBOXYMETHYLATION OF CELLULOSE WITH CHANGE OF CONCENTRATION OF REAGENTS*

Monochloroacetic acid				
Solution strength (%)	Weight per gram of cellulose (g.)	Residual sodium hydroxide (%)	Copper in product (%)	Ratio of acid groups to glucose units
50	0.5	10.0	0.33	1:60
50	0.5	20.0	1.59	1:13
50	0.5	28.0	2.95	1: 6
50	0.5	33.4	4.51	1: 4
50	0.5	38.0	5.41	1: 3
10	0.1	33.4	1.19	1:17
20	0.2	33.4	1.67	1:12
30	0.3	33.4	2.40	1: 6.5

* Time of reaction, 1 hour; temperature, 25°C.

percent copper, or about 1 acid group per 4 glucose units.

Under these conditions change of time of treatment between 1 and 5 hours had little effect, and 3.1 percent copper was obtained after ½ hour of treatment. Room temperature (25° C) was most favorable, the copper content dropping to 1.97 percent at 10°, and 3.96 and 3.42 percent at 50° and 75°, respectively. When the order of addition was reversed—that is, when the cellulose was first swollen with alkali and then treated with a solution of chloroacetic acid—the copper content of the salt decreased and results were quite erratic, varying from 0.30 to 2.2 percent of copper. The use of sodium chloroacetate without excess caustic, either 13 percent in 60-percent ethyl alcohol or 42 percent in water, gave very little substitution, yielding products containing less than 0.25 percent copper. Table II shows the effects of varying concentrations of acid and alkali on the degree of substitution, the latter having the greater effect.

In the commercial treatment of either cloth or yarn, it would be advantageous to be able to add sodium chloroacetate to mercerizing caustic and thus make use of a one-bath process. Cellulose was treated with a 20-percent sodium hydroxide solution containing 6.7 percent sodium chloroacetate (which corresponds to the second example in Table II), and the copper content was found to be 2.01 percent instead of 1.59 percent. This method has two disadvantages, however, in that the sodium salt is not very soluble in concentrated alkali and also, as has been shown by Berhenke and Britton [4], it hydrolyzes rapidly, reaching a rate of 5.8 percent per minute at pH 13. It is more practical, therefore, to impregnate the cotton cellulose with the desired amount of acid and then with strong sodium hydroxide solution in which the salt produced is relatively insoluble.

In order to examine the swelling characteristics of partially carboxymethylated cotton fiber, 2 grams of lint cotton (Rowden variety) were extracted with hot alcohol, soaked in 20-percent chloroacetic acid, removed wet, air-dried, and then treated for 1 hour with 42-percent sodium hydroxide solution. The alkali was then washed out with 95-percent ethyl alcohol to avoid swelling the fibers. Analysis showed the fiber to have about 1 carboxyl group per 5 glucose units. When these fibers were placed under the microscope and swelled with water, they showed the "ballooning" phenomenon which is commonly associated with the action of cuprammonium solution on cotton fiber [14] (see Figure 1). This fact is of interest because it is the first time, to our knowledge, that ballooning has taken place with water as a swelling agent. The ballooning also shows that at least part of the primary wall has been left intact by the treatment. The fiber may be dehydrated and shrunk with alcohol, and swelled with water, alternately, a number of times. Eventually the primary wall cracks off and the fiber does not balloon but swells more or less uniformly to about three times its original diameter. The slightly gelatinous state of the fiber indicates that this degree of substitution is too high for practical use.

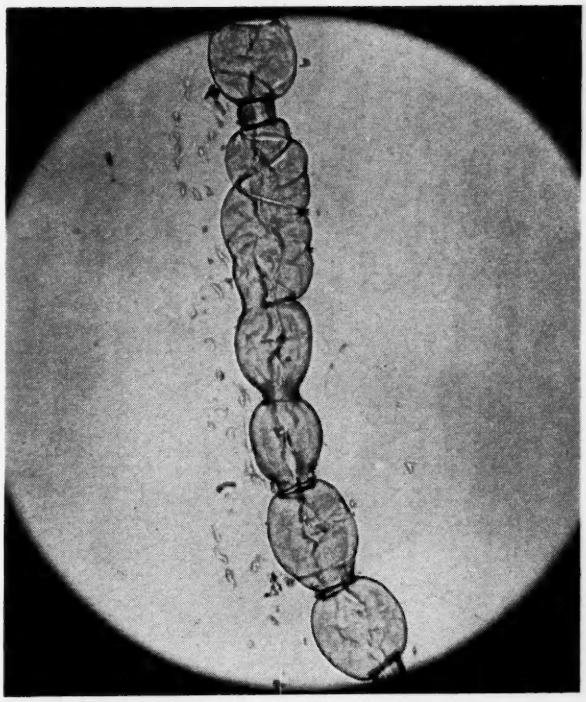

FIG. 1. *Partially carboxymethylated cotton fiber, swollen with water.*

Actual physical measurements of swelling of treated fibers by microsectioning were not made mainly because of the difficulty of obtaining a suitable imbedding material for cross-sectioning. However, swelling was observed under the microscope by placing a slide of dry fibers (unmounted) in the field and allowing water to seep under the cover glass. From visual observation it may be stated that swelling varied with the amount of substitution of carboxymethyl groups, varying from a slight amount of swelling in the lightly treated fibers to ballooning in the heavily carboxymethylated fibers.

FIG. 2. *Cross section of cotton yarn, dyed with methylene blue to show uneven carboxymethylation.*

Partial Carboxymethylation of Yarns and Threads

The partial carboxymethylation of a yarn involves not only adjustment of the conditions of treatment so as to give the desired average substitution, but this substitution must also be fairly uniform throughout the yarn. A typical preparation was as follows:

Cotton sewing-machine thread, 12/5, was made into a small skein weighing about 45 grams and hot ethyl alcohol was used to remove the waxes as an aid to wetting during the treatment. The skein was dried and then padded with an equal weight of a 3-percent solution of chloroacetic acid containing about 0.05 percent of a wetting agent. The skein was then air-dried in front of a fan at room temperature. The acid had little effect upon the breaking strength of the thread as long as the temperature of drying was below 60°C. The skein of thread was then treated under tension at constant length, in the usual manner for mercerization, using about 100 milliliters of 35-percent sodium hydroxide. After 1 hour, the skein was washed first in cold water and then in hot. When this thread was treated with 10-percent cupric sulfate solution and washed, the copper content was 0.79 percent, or about 1 carboxyl per 25 glucose units. Variation in conditions gave the results shown in Table III. Samples D and E were treated to the point where they became slightly gelatinous when wet, with consequent loss of strength. The others lost very little strength.

Two methods for determination of the degree of uniformity of treatment were used. The first consisted of impregnating the yarn with cupric sulfate solution, which formed the insoluble copper salt of carboxymethylcellulose, then washing thoroughly and precipitating the copper *in situ* with a solution of potassium ferrocyanide, simultaneously forming the potassium salt of the carboxymethylcellulose. This alternate treatment with cupric sulfate and potassium ferrocyanide may be repeated several times, the copper content increasing almost uniformly with each cycle. The distribution of the copper in the fiber may be observed microscopically to determine evenness of treatment. A second, and preferred, method consisted of dyeing the yarn by boiling for 30 minutes with 0.1-percent solution of methylene blue in 0.1-percent acetic acid and then washing with hot water. Untreated cotton was colored only slightly while the carboxymethyl cotton dyed a deep blue. Figure 2 shows a cross section of a dyed thread which was purposely undertreated to show the necessity of thorough impregnation of reactants. It will be observed that the outer fibers, which dye a deep blue, have been treated to the point of partial solubility, whereas the innermost light-colored fibers are practically untouched.

The intensity of blueness obtained when dyeing carboxymethylated cotton with methylene blue is also a good visual indication of degree of treatment. The yarns and fibers which were lightly treated (about 1 carboxymethyl group per 40 to 50 glucose residues)

TABLE III. PREPARATION OF CARBOXYMETHYL COTTON SEWING THREADS*

Sample	Monochloroacetic acid per gram of cotton (g.)	Strength of residual sodium hydroxide solution (%)	Copper equivalent (%)	Ratio of acid groups to glucose units	Breaking strength (lb.)
Control	—	—	—	—	11.0
A	0.01	35.0	0.62	1:30	10.8
B	0.03	34.9	0.79	1:25	10.3
C	0.06	34.9	1.25	1:16	10.1
D	0.09	34.8	1.91	1:10	8.3
E	0.12	34.8	2.28	1:07	6.5

* Extracted with hot ethyl alcohol to remove waxes prior to treatment.

dyed light blue while cotton which had been treated to contain approximately 1 carboxymethyl group per 5 to 10 glucose residues dyed a very deep blue. Samples in between these two ranges dyed with intensities varying directly with the severity of the treatment.

Swelling and Absorbency Properties of Treated Yarns

Two methods for determining the water-absorbency and swelling capacity of cotton fibers now being developed in this Laboratory were made use of in an attempt to estimate these properties in the carboxymethylated cotton. Samples were tested for comparative water-absorption by soaking in water containing a wetting agent for 24 hours and then centrifuging at 1,850 times gravity for 20 minutes, after which residual moisture was determined. Swelling of fibers was tested by an "orifice test" [22] in which a sufficient number of yarns were placed lengthwise in an orifice—so that about 34 percent free air space remained—and the water leakage was determined for two successive 10-minute periods under 50 pounds' water pressure. The comparative swelling and water-absorbency characteristics of cotton treated to various degrees of substitution are illustrated by the data shown in Table IV. The results indicate the high absorbency and swelling properties of the material and show that as little as approximately 1 carboxymethyl group per 40 glucose units imparts good swelling properties.

When the treated and control samples of yarn were dried at 105°C for 16 hours and then allowed to come to equilibrium at 65 percent relative humidity and 21°C, the moisture content of the treated material was not greatly different from that of the mercerized control. The untreated cotton had a moisture content of 6.8 percent, and the mercerized control 9.6 percent, whereas the treated sample with a copper equivalent of 1.13 percent (about 1 carboxymethyl group per 18 glucose units) contained 10.3 percent moisture. A number of salts from commercial carboxymethylcellulose were prepared and conditioned as above, but the moisture contents did not vary greatly. The results (in percent moisture) on each salt were as follows: sodium, 11.3; copper, 11.0; aluminum, 11.1; calcium, 11.5; lead, 12.2; and barium, 10.9.

Resistance of Carboxymethyl Cotton to Microbiological Attack

The excellent resistance of partially acetylated cotton [13] to microbiological attack encouraged the hope that the partially carboxymethylated cotton would also be immune. Preliminary tests showed that this was not so and the treated material degraded as rapidly as the original cotton. Partially acetylated cotton has approximately 1 acetyl group

TABLE IV. SWELLING AND WATER-ABSORBENCY PROPERTIES OF PARTIALLY CARBOXYMETHYLATED COTTON YARNS

Sample	Copper equivalent (%)	Ratio of acid groups to glucose units*	Water-absorbency (%)	Leakage at 50 lb. pressure, 1st 10 min. (ml.)	Leakage at 50 lb. pressure, 2nd 10 min. (ml.)	Breaking strength, Dry† (lb.)	Breaking strength, Wet‡ (lb.)
Untreated cotton	0.03	—	—	11.33	10.30	1.7	2.1
Mercerized control	0.19**	—	50.7	7.33	6.53	2.1	2.4
Carboxymethyl cotton sodium salt	0.50	1:40	75.8	0.46	0.40	2.3	2.6
Carboxymethyl cotton sodium salt	0.72	1:25	98.1	0.0	0.0	2.4	2.2
Carboxymethyl cotton sodium salt	2.44	1:8	181.8	0.0	0.0	2.1	0.8§
Carboxymethyl cotton copper salt	2.44	1:8	116.9	0.33	0.29	2.2	1.8

* Not corrected for any substitution due to oxidation of cellulose.
† Standard conditions [1].
‡ Determined as before except with wet yarn to show wet strength.
** Apparently due to some oxidation of the alkali cellulose during mercerization.
§ Microscopic examination of this sample indicated that sufficient softening of the fibers took place so that they were partially bonded together on drying. When wet, the fibers were slightly gelatinous, which probably explains the low wet strength.

TABLE V. RESISTANCE OF CARBOXYMETHYLATED COTTON SEWING THREAD TO MICROBIOLOGICAL ATTACK

Sample	Metal content (%)	Pounds breaking strength after time indicated: Days exposed in burial test										Days exposed in Bayou St. John, New Orleans, La.*									
		0	4	7	11	14	17	21	28	42	56	70	84	3	7	10	14	17	21	24	28	35	49	70
Blank	—	10.0	0.9	0.5	—	—	—	—	—	—	—	—	—	8.3	2.8	1.9	1.0	—	—	—	—	—	—	—
Mercerized control	—	10.3	4.2	1.7	1.2	—	—	—	—	—	—	—	—	9.2	5.5	3.3	2.0	2.3	—	—	—	—	—	—
Copper naphthenate control	1.67†	10.7	10.8	9.9	10.4	10.5	10.6	10.5	11.1	10.7	10.0	6.4	2.0	10.4	9.7	7.5	7.0	7.1	7.5	4.7	6.1	4.5	3.5	1.5
Aluminum salt	0.15	10.3	6.8	0.7	2.0	1.6	1.2	—	—	—	—	—	—	8.8	4.3	2.7	5.4	1.1	4.4	2.4	1.8	—	—	—
Copper salt	0.89‡	11.6	9.9	11.4	10.2	9.5	9.4	10.0	9.1	6.3	—	—	—	10.0	9.9	7.9	6.3	5.8	3.7	3.8	2.8	—	—	—
Mercury salt	0.95	11.3	10.2	10.4	11.3	11.3	10.6	10.6	10.6	10.5	6.0	4.3	—	10.1	10.0	8.3	5.6	5.5	3.4	3.4	2.7	5.2	—	—
Lead salt	2.95	10.7	6.6	4.1	2.0	6.0	4.8	2.9	—	—	—	—	—	10.5	10.4	7.7	3.7	4.6	3.9	2.1	—	—	—	—
Silver salt	0.46	11.4	10.5	10.5	10.0	3.4	1.2	—	—	—	—	—	—	10.1	11.0	10.8	9.7	9.1	8.6	6.6	6.7	3.9	2.5	1.5

* Temperature varied from 85°F to 68°F. Average temperature was 76.9°F.
† The usual amount of copper in copper-naphthenate-treated material is approximately 1 percent.
‡ The approximate number of carboxymethyl groups equaled 1 in 25 glucose residues based on copper content.

per glucose residue, whereas carboxymethylated cotton has only 1 in 7 or less, and this difference may explain the lack of rot-resistance in the latter. Insoluble salts, however, are easily formed by treatment of the carboxymethylated cotton with metals as described above, and a number were prepared and tested. One set of threads was immersed in the brackish water of Bayou St. John, New Orleans, Louisiana, and a second set was tested by a burial test similar to that described by Dean, Strickland, and Berard [9]. The former was arranged in loose skeins fastened to a cord which was weighted so that the threads were always below the surface of the water. The latter test was modified in that 8-inch lengths of thread were stapled warpwise to two 6-inch pieces of cypress wood and buried in the same manner as the cloth samples ordinarily used. Samples were removed at intervals and breaking strengths determined by the standard A.S.T.M. method for cotton yarns [1] except that 10 breaks were made on samples of 3-inch length. Results of these tests are given in Table V.

The small number of samples broken each time, along with some nonuniformity in treatment, accounts for the minor discrepancies in the results for some of the series; but, in general, the trend is quite clear. The rapid degradation of the controls in approximately 1 week or less illustrates the activity of the microorganisms. The protection given by copper naphthenate is approximately what would be expected of such treatment and comparison with the carboxymethylated cotton shows that the latter has practically no commercial possibilities. As might be expected, copper, silver, and mercury all offer considerable protection whereas aluminum and lead do not. Differences between results in the burial beds as compared with those obtained from the Bayou samples are probably due to differences in solubility in the constant leaching by the brackish Bayou water as compared to static conditions existing in the burial beds.

Neish, Ledingham, and Mackey [19] have found that the relatively insoluble salt of copper with dimethylglyoxime, if precipitated in cloth, will render it rot-resistant. For this reason, the samples containing double and triple quantities of the insoluble cupric ferrocyanide, prepared by alternate treatment with cupric sulfate and potassium ferrocyanide, in a manner similar to that used for determining uniformity of treatment, were tested by the burial proce-

dure. The cupric ferrocyanide gave little or no rot-resistance.

Conclusions and Summary

A quickly swellable cotton fiber may be obtained by partial carboxymethylation to such a degree of substitution that the fiber does not lose strength but does swell when wet. Such carboxymethylation is obtained by the impregnation of cellulose with a solution of monochloroacetic acid followed by treatment with a strong solution of sodium hydroxide yielding the sodium salt of carboxymethylcellulose. Degree of substitution may be varied by change in conditions. The degree of substitution is conveniently estimated by preparing the insoluble copper salt of the carboxymethylcellulose and then determining the copper content. With degrees of substitution of about 1 acid group per 15 glucose residues or less, the treated yarns do not vary greatly in breaking strength, feel, appearance, or moisture content from mercerized controls. Swelling capacity and water retention, however, are greatly increased. The treated cotton shows different dyeing characteristics from untreated cotton. Although the addition of small amounts of carboxymethyl group to the cellulose molecule does not protect it from microbiological attack, addition of copper, silver, or mercury, to form the corresponding insoluble salt of carboxymethylcellulose, imparts considerable resistance to such attack.

Acknowledgment

Thanks are due to Miss Mary L. Rollins and Miss Ines V. deGruy for the microsections and photographs; to Dr. Carl M. Conrad and Miss Hilda M. Ziifle for the water-absorbency measurements; to Mr. Charles F. Goldthwait and Mr. Alton L. Murphy for the orifice tests; and to Mr. Wilson A. Reeves and Mr. Lamont Hagan for some of the metal analyses.

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Acetylation of Zein Fibers

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Abstract

The acetylation of zein fibers increased the water-resistance, improved the softness of the fiber by moderation of the severe formaldehyde post-cure, improved the boil-resistance, whitened the fiber by removal of pigments, and decreased the dye uptake. Acetylation was accomplished with acetic anhydride, with sodium acetate or sulfuric acid as catalyst. Acetyl contents of more than 5 percent were quickly obtained in continuous-processing equipment. The amount of acetyl groups introduced can be regulated by changing the composition, time of reaction, or the temperature of the acetylating mixture.

THE acetylation of azlon fibers is generally beneficial, as has been shown by various workers. Atwood [1] has reported that acetylation improves the water-resistance of casein fiber (Aralac) and retards the rate of dye uptake so that it approaches that of wool. Brown *et al.* [2] introduced up to 9 percent acetyl groups in casein fiber by treatment with acetic anhydride. They discussed the effect of various degrees of acetylation on the rate of dye uptake and water-resistance. Improvements similar to those obtained for casein are claimed for peanut protein fibers in two British patents [7]. A United States patent by Veatch [8] discloses the addition of as much as 6.8 percent acetyl groups to powdered zein when acetic anhydride is used with sulfuric acid as a catalyst. In the Veatch patent sodium acetate was described as being less effective, whereas Brown [2], working with casein, found no catalyst that was very effective in accelerating the reaction. It is generally known that the type of catalyst influences the course of the acetylation [6]. Acid catalysts favor the formation of the *O*-acetyls and basic catalysts promote *N*-acetylation. Also it is known that *O*-acetyl groups are very labile to weak alkali [5].

For this report the effect of acetylation on the various properties of zein fibers has been investigated, together with studies establishing the conditions and factors for acetylation. A technical grade of acetic anhydride was used in these studies because of its low cost and because of its effectiveness in acetylation. Acetylation was briefly mentioned in a previous publication [3] describing the production of high-strength textile fibers by the wet spinning of an alkaline zein dispersion. Since the earlier report, the zein fiber process has been modified to permit the first formaldehyde cure (precure) to be done continuously. This is accomplished in equipment similar to that described in the following process for continuous acetylation.

Method of Acetylation

Acetylated zein fibers were prepared by a continuous process in semi-pilot-plant equipment. Figure 1 is a photograph of the apparatus showing the large U-tube which contained the acetylating mixture, the temperature of which was controlled by an external oil bath. The composition of the acetylating mixture was varied, as will be discussed later. The tow of dry fiber (after precure and stretch) was fed at a constant rate from a wooden roller into one end of the acetylating tube. When large tows of about 15,000 denier were used, it was preferred that they have little or no twist to facilitate washing after the treatment. The fiber tow entered the tube through a funnel, which also served as the entrance for the circulating acetylating mixture. By this arrangement, the liquid flowing down through the funnel carried the fiber tow along with it, keeping the tow taut between the feed roller and the funnel. The fibers generally swelled in cross section and decreased in length in the acetylating mixture. The resulting

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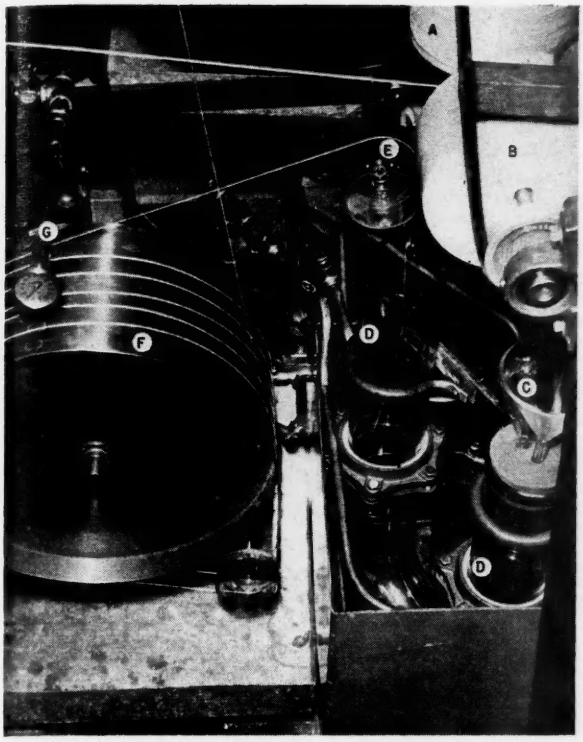

FIG. 1. *Photograph of continuous acetylating apparatus. A—Supply package. B—Wooden feed roller. C—Feed funnel. D—U-tube. E—Idler roller (does not touch wooden feed roller). F—Wash drum. G—Sprayer.*

rope-like tow piled up at the bottom of the tube in haphazard fashion. After the time lag desired for the treatment, the tow was withdrawn continuously from the discharge end of the tube. The rate of withdrawal was adjusted to allow for shrinkage of the fiber during acetylation; hence the time of treatment remained constant during a run.

The acetylated fiber tow was pulled from the tube by a large stainless-steel drum around which it traveled several times while being advanced across the drum by a small offset glass roller. The tow was washed by a spray of cold water over the large drum and then it passed to a second drum, across which it was similarly advanced while being washed with warm (50°C) water.

After these two washings the fiber was stretched and cured under tension in strong formaldehyde solution. The curing was accomplished while the fiber traveled 25 to 40 times around a set of two hard rubber rollers mounted 4 feet apart on a stainless-steel frame. The fiber tow was advanced along the rollers and kept separate by a series of guides along the incoming side of each roller. The whole frame was submerged in 10-percent formaldehyde heated to about 60°C and the reaction was catalyzed with ammonium chloride or sulfate. The pH was adjusted to 1 by adding the corresponding acid. The usual time for a point on the continuously moving tow to travel through the bath was 15 to 45 minutes—depending on the number of wraps and the speed of reels. One roller of the frame was driven, thereby exerting a pull on the incoming wet fiber tow, which stretched about 100 to 150 percent. The tow was next advanced across drums while being washed with water and then dried in the continuous drier previously described [3].

To facilitate fiber processing through the acetylating and post-curing steps a fiber having a precured formaldehyde content of about 1 percent is desirable. For the acetylating studies reported in this paper, fibers containing 0.8 to 1.0 percent of formaldehyde were used. The final formaldehyde contents after acetylation and post-curing were usually about 3.5–4.0 percent. Studies showing the effect of various formaldehyde contents on fiber processing and their relationship to the fiber properties will be presented in a future publication.

Factors Influencing Amount of Acetylation

The important factors influencing the amount of acetylation were the catalyst, the composition of the mixture, and the time and temperature of the treatments. Figure 2 shows acetyl content versus time curves for various formulas at 85°C. All temperatures reported are those of the external oil bath; the temperature of the circulating acetylating mixture at the entrance end of the tube was 5° to 10° lower. In all experiments, except when relatively pure acetic anhydride was used, acetic acid was an important component. The acid promoted swelling of the fiber, and caused a decrease of about 50 percent in the length of the tow. Almost invariably, this phenomenon seemed necessary for successful continuous withdrawal of the fiber. Also, when sodium acetate was used as a catalyst, acetic acid helped to keep it in solution. A desirable concentration was 5- to 10-percent acetic acid. The acid concentration was kept constant by replacing the mixture withdrawn by the swollen tow with a mixture relatively low in acetic acid from a reservoir which kept the volume of acetylating liquid constant. A higher concentration

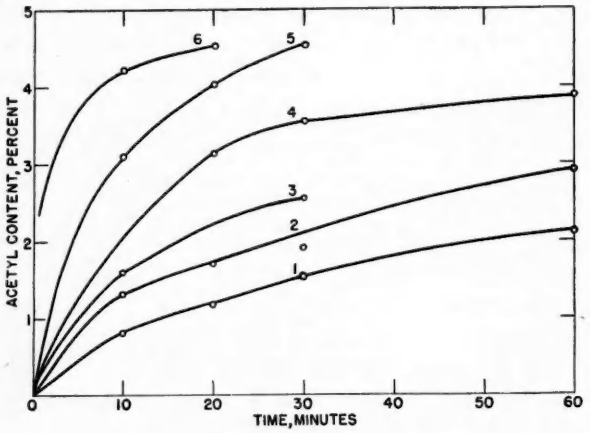

FIG. 2. *Curves for acetyl content of zein fibers versus time of acetylation. 1—45% acetic anhydride (tech. 95%), 50% dioxane, and 5% acetic acid at 85°C. 2—95% acetic anhydride (tech. 95%) and 5% acetic acid at 85°C. 3—100% acetic anhydride (tech. 95%) at 85°C. 4—100% acetic anhydride (tech. 95%) at 100°C. 5—90% acetic anhydride (tech. 95%), 5% acetic acid, and 5% sodium acetate at 70°C. 6—90% acetic anhydride (tech. 95%), 5% acetic acid, and 5% sodium acetate at 85°C.*

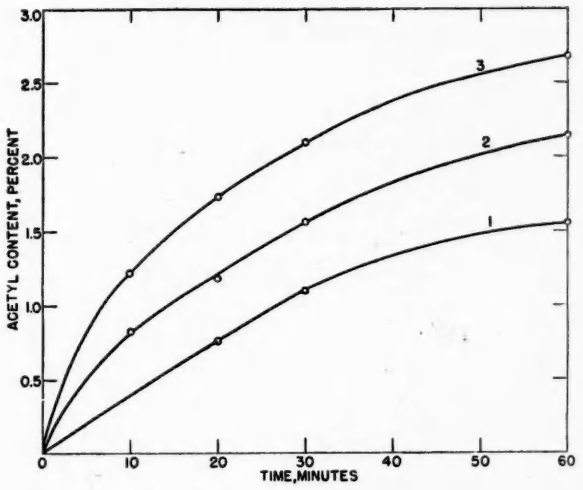

FIG. 3. *Curves for acetyl content of zein fibers versus time of acetylation in 45% acetic anhydride (tech. 95%), 50% dioxane, and 5% acetic acid. 1—At 70°C. 2—At 85°C. 3—At 100°C.*

of acetic acid was undesirable because the acetylated tow became too swollen and too weak to be withdrawn from the tube. Moreover, the acetyl content of the fiber decreased somewhat, probably because of the diluting effect of the acid.

In some experiments, the acetic anhydride-acetic acid mixture (10-percent acetic acid) was diluted with an equal volume of dioxane or toluene. Curve 1, Figure 2, shows a decreased acetyl content when dioxane was used as the diluent, as compared to curve 2, for no diluent. The curves in Figure 3 are for the dioxane mixture at 70°, 85°, and 100°C.

Catalysts have a marked effect in increasing the rate of acetylation of zein fibers. As shown in Table I, the use of either sodium acetate or sulfuric acid in acetylating mixtures (at 65°C—20 minutes) produces fibers having a relatively high acetyl content. The acetyl content of a fiber treated in a mixture of acetic anhydride and acetic acid was 1.64 percent; under the same conditions, but with 1 percent sodium acetate also present, the content was increased to 4.13 percent. Sulfuric acid was even more effective. A 0.1-percent sulfuric acid mixture resulted in a 5.54 percent acetyl content in 20 minutes and increased it to 6.61 percent in a 30-minute treatment. In fact, acetylation was too rapid to control under our continuous acetylating conditions. A 0.4-percent sulfuric acid mixture at 65°C swelled and tenderized the tow so much that the filaments were plastered together and were too weak to be handled. A 2-percent sulfuric acid mixture dissolved the fiber almost immediately. Although sodium acetate also increased the swelling of zein fibers to some extent, its use as a catalyst was easily adapted to our process. A relatively longer time, such as 30 minutes, and milder temperatures were preferred in our operation so that any slight error in coordinating reel speeds did not have a pronounced effect on the amount of acetylation. However, the more rapid reactions show good promise for development of a continuous, commercial process. Curve 6 in Figure 2 is for a 5-percent sodium acetate mixture at 85°C and the curves in Figure 4 give the acetyl content versus time for 1-percent sodium acetate mixtures at 50°, 60°, and 70°C.

TABLE I. ACETYL CONTENTS OF FIBERS FROM ACETIC ANHYDRIDE-ACETIC ACID

Catalyst	Time (min.)	Temperature (°C)	Acetyl content (%)
None	20	65	1.64
1.0% NaOAc	20	65	4.13
0.1% H_2SO_4	20	65	5.54
0.1% H_2SO_4	30	65	6.61
5.0% NaOAc	20	70	4.02
5.0% NaOAc	20	85	4.52

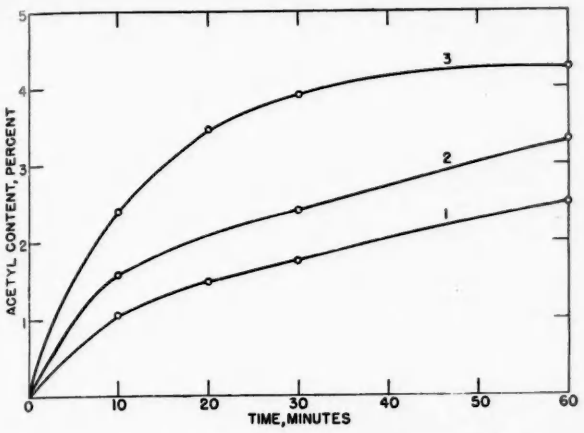

FIG. 4. *Curves for acetyl content of zein fibers versus time of acetylation in 94% acetic anhydride (tech. 95%), 5% acetic acid, and 1% sodium acetate. 1—At 50°C. 2—At 60°C. 3—At 70°C.*

Analysis for Acetyl Groups

The micro-method described by Elek and Harte [4], with slight modifications in the method of collecting and titrating the distillate, was used for the determination of acetyl groups in the fibers. This method was desirable for routine analysis because of the accuracy, ease of manipulation, and low blank values.

The fiber samples were first extracted overnight with acetone over sodium hydroxide in a Soxhlet extractor. This preliminary extraction was important because unextracted samples ran 5 to 15 percent higher in apparent acetyl content.

A 70- to 80-milligram fiber sample was hydrolyzed for 1 hour with 5 milliliters of a 25-percent aqueous *p*-toluene sulfonic acid solution. No difference was noted between 1, 2, or 3 hours of hydrolysis. The receiving flask was charged with 10 milliliters of carbon-dioxide-free distilled water containing 1.5 grams of neutral potassium iodide. After the acetic acid was distilled, 5 milliliters of a 4-percent solution of potassium iodate were added and the liberated iodine was titrated in the usual manner with 0.02*N* thiosulfate. Blank determinations on unacetylated zein fibers ran approximately 0.15 to 0.20 percent acetyl content. The values reported have been corrected for their respective blanks and moisture content. Duplicate determinations had an average percentage error of 2.9 percent, which is very satisfactory for samples of this nature.

Effects of Acetylation

When zein fibers are acetylated, washed, and dried while being held at constant length they lose from 15 to 30 percent of their dry strength. However, in the process just described, when the fiber was relaxed during acetylation and then restretched 50 to 150 percent, the acetylated fibers had dry strengths equal to or as much as 10 percent greater than the nonacetylated fibers. The wet strengths were in-

TABLE II. PROPERTIES OF FIBERS

General properties		Zein fibers No. 1	No. 2	No. 3	No. 3a	No. 4	Wool 50–60s
Strength (g./den.)	Dry	1.49	1.25	1.45	1.25	1.20	up to 1.30
	Wet	0.74	—	0.71	0.72	0.63	—
Shrinkage (%) 15 min. boil	Water	19	16	12	—	12	—
	Alkali	11	9	9	3	7	—
Strength after boil in water (g./den.)	Dry	1.06	0.95	1.10	—	1.00	—
	Wet	0.58	—	0.60	—	—	—
Denier		3.42	4.27	2.20	2.70	1.36	—
Acetyl content (%)		5.33	3.98	3.00	—	3.31	—
Formaldehyde content (%)		3.16	4.19	3.72	—	3.71	—
Load-elongation properties							
Final elongation (%)		15	20	15	20	20	20
Load for elongation (g./den.)	Dry	0.98	0.81	1.07	0.75	0.90	0.72
	Wet	0.45	0.31	0.47	0.41	0.47	0.32
Temporary set (%)	Dry	9.4	14.1	8.9	14.8	13.9	12.0
	Wet	5.9	9.6	5.6	11.1	10.0	0.0
Young's modulus (g./den./%)	Dry	0.27	0.27	0.32	0.27	0.30	0.22
	Wet	0.041	0.030	0.051	0.041	0.043	0.11

creased between 20 and 40 percent. As a typical example, a fiber having a dry strength of 1.2 g./den. and a wet strength of 0.5 g./den., after acetylation at constant length had strengths of 1.01 and 0.52, respectively, but after restretching they had strengths of 1.33 and 0.63 g./den., respectively.

Although acetylation increases the wet strength of zein fibers and improves their water-resistance, it is not a remedy for shrinkage. Zein fibers must be stretched to obtain high strengths (up to 2.0 grams per denier) and the stretched fibers, whether acetylated or not, return to their unstretched length when plasticized with warm water. The second formaldehyde cure (post-cure) given to the fiber while it is held under tension reduces these shrinkages, even in boiling water (see Table II), to acceptable values. The treatment in formaldehyde causes some loss in strength, but this loss is usually much greater and harder to control if the fibers are not first acetylated. Although fibers of good appearance have been produced by eliminating the acetylating step and using milder post-cures, the use of acetylation moderates the reaction with formaldehyde so that better fibers result. It may be that acetylation binds groups in the protein molecule which otherwise would react with formaldehyde. In fact, the usual formaldehyde post-cure on nonacetylated fibers is so severe that the filaments become brittle and are usually plastered together, whereas acetylated fibers separate readily when dry and have a soft feel.

Another advantage of the acetylation step is the extraction from the fibers of the yellow pigments and xanthophyll oils which occur in the raw protein. These pigmented oils are readily removed from the swollen fibers by the acetylating mixture in which they accumulate. The resulting fibers are sufficiently white to take any shade of dye.

Acetylated fibers are much more resistant to boiling acid dye baths than the nonacetylated fibers. Like other protein fibers, acetylated zein has a decreased affinity for wool dyes, thus making more uniform dyeing possible.

Properties of Finished Fibers

Table II lists some of the more important properties of representative zein fibers which have been acetylated and post-cured in formaldehyde as described above. Final strengths up to 1.5 g./den. dry and 0.75 g./den. wet have been obtained.

The fibers have good resistance to boiling in alkaline solutions, but are much less resistant to boiling acid. This poor resistance to acids is to be expected when formaldehyde, which forms acid-labile linkages, is used as the curing agent. Boiling in acid can be circumvented by using dyes which can be applied in alkaline or neutral baths. Provided alkaline dye baths are used, zein fibers are stable during long periods of boiling (30 minutes–2 hours). Practically all shrinkage occurs in the first few minutes of boiling.

Results of preliminary dyeing experiments indicated that acetylated zein fibers can be dyed with all types of dyes. Good tinctorial values were obtained. Fibers dyed in boiling neutral dye baths had shrinkages of 10 to 20 percent. However, when alkaline dye baths were used, this shrinkage was reduced by more than 50 percent. If yarn shrinkages prove to be excessive, a preshrinking treatment by washing in mild alkali and relaxing in live steam can be given to the fibers. Such a treatment results in approximately 10 to 15 percent loss in strength of the fiber and changes in other properties, as shown in Table II, which include the properties of a finished fiber (No. 3), and of the same after the alkali and steam treatment (No. 3a). Data on wool are included for comparison.

High temperatures were preferred in dyeing zein fibers because better exhaustion of the dye bath and better penetration of the dye were obtained. Fibers dyed at low temperatures (below 70°C) had poor wash-resistance and tended to crock—indicating poor penetration of the dye.

The finished fiber gives a weak color reaction with Millon's reagent as compared to a very dark red for nonacetylated fibers. After the acetylated fiber is boiled in dilute alkali, the color of the test is more pronounced than for the nonboiled fiber, showing that *O*-acetyl groups, which are alkali-labile, are being hydrolyzed from acetyl tyrosine [5]. Two samples of fibers having 4.8 percent and 2.13 percent acetyl content lost about 30 percent of these values when heated at 98°C for 30 minutes in a buffer at pH 8. The effect of this loss of *O*-acetyl groups has not been fully investigated, but such a loss does not seem to alter the properties of the zein fiber to any great extent.

Acknowledgment

The authors wish to express appreciation to the Harris Research Laboratories for determining the

load-elongation properties of zein fibers, and to Miss Levon A. Merchant, formerly of this Laboratory, for assisting with the acetyl determinations. We also wish to thank the E. I. du Pont de Nemours & Company, Inc., and the Calco Chemical Division, American Cyanamid Company, for their cooperation in evaluating the dyeing properties of zein fibers.

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Nitrogen Content of Cotton in Relation to Other Fiber Properties

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COMMERCIAL cottons show notable differences in their physical properties not only between varieties and production centers but also between years and successive pickings within years. There are also variations in some of the chemical constituents of cotton fibers, about which a number of investigators have obtained information. Whether or not broad or useful index relations, causal or other, exist between any of these chemical and physical properties has thus far remained largely unknown. There is, however, enough suggestive material in the literature and in existing knowledge of the developmental processes of the lint cell to provide an interest in the subject.

During the process of secondary thickening of the wall of the lint cell each successive cellulose deposition on its inner surface reduces the volume of the protoplast. If the composition of the protoplasm of the lint cell were assumed to be fairly constant with respect to nitrogen, or some other constituent, it would follow that the concentration of this constituent, in terms of the weight of the entire fiber, should provide an index to lumen volume relative to wall thickness. It was to test this relationship that the investigation reported in this paper was originally undertaken by means of nitrogen determinations on 38 upland samples of various varieties and sources. These results indicated not only that there was some relationship between total nitrogen in lint samples and the percentage of immature fibers, but also that there was a substantially better correlation between lint-nitrogen and fineness—that is, nitrogen tended to increase as the weight-per-inch of fibers decreased. To provide a more adequate basis for conclusions, the investigation was extended to include a total of 248 upland and 66 Sea Island cottons. The data resulting from these measurements are reported, after which attention is turned in this paper to the effects on nitrogen accumulation in lint of such factors as drought, shade, various kinds of plant mutilations, and its relationship with nitrogen and carbohydrate levels in the leaves and other parts of the plant.

The upland and Sea Island cottons were drawn at random from sample stocks accumulated from those submitted for fiber and yarn property measurements by various Federal and State Agricultural Experiment Stations to the Cotton Branch of the Production and Marketing Administration. The data on fiber and yarn properties were taken from the processed reports of the Production and Marketing Administration. The upland samples originated in a total of 23 production centers distributed over the four cotton-producing regions of the United States, as follows: Southeast 7, Midsouth 7, Texas-Oklahoma 6, and Far West 3. The crop years 1941, 1942, and 1943 were represented, with the exception that only 1941 and 1942 samples from the Far West were included. The long-staple cottons (all but 4 were Sea Island) originated from four Southeastern stations during 1942 and 1943.

For the calculation of correlation coefficients (Table I) between nitrogen and various fiber and yarn properties and, by covariance analyses, the separate contributions of heredity and environment, use was made of 158 of the upland and 49 of the Sea Island samples. These samples represented varieties or strains that were grown in two or more station-years and those from station-years within which two or more varieties were grown.

Review of Literature

Ivanova and Kurennova [6] traced changes in the composition of cotton lint (variety Naviotskii) from 25 days after flowering through to open bolls. Total nitrogen, referenced to dry weight of lint, decreased from 1.09 percent in 25-day-old bolls to 0.18 percent in open bolls. Water extracts, also referenced to dry weight of lint, contained reducing substances

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† This paper has been approved by the Director as Technical Paper No. 998.

that decreased from 19.3 percent in 25-day-old bolls to 2.1 percent in open bolls. Phosphoric anhydride decreased from 0.30 to 0.13 percent. These investigators reported finding no starch in the lint cells of cotton. Farr [5] likewise found no evidence of starch in the plastids of developing cotton fibers. Furthermore, Farr's photomicrographs of lint cells of cotton show no evidence of vacuoles and the writer was advised by her that she had never been able to observe any indications of such vacuoles.

Ridge [10] and Geake [7], respectively, have reported on the percentages of total nitrogen and of phosphoric acid in cottons from various sources, as follows:

Cotton	Nitrogen (%)	P_2O_5 (%)
American	0.204 to 0.221	0.042 to 0.061
Sea Island	0.262 to 0.290	0.057 to 0.068
Egyptian	0.290 to 0.317	0.077 to 0.314
South American	0.184 to 0.277	0.054 to 0.077
Indian	0.180 to 0.280	0.054 to 0.124
Egyptian:		
Combed sliver	0.228	0.116
Comber waste	0.274	0.159
Sea Island:		
Combed sliver	0.209	0.057
Comber waste	0.306	0.098

More recently Nickerson, Fontaine, and Leape [8] have pointed to a close relationship between total nitrogen and fineness in seven variety samples of cotton grown at Stoneville, Miss. Ash alkalinity, wax, and pectate in lint also tended to increase with fineness. Essentially no difference was found between the concentrations of organic ammonia nitrogen (0.163 percent) and total nitrogen (0.166 percent). This contrasts with results reported by Ivanova and Kurennova [6].

Concerning the weight of fresh fiber, Compton and Haver [3] found that the concentration of reducing sugars in field-grown cotton lint decreased from 8.4 percent 10 days after flowering to 0.8 percent at 30 days, 0.5 percent at 35 days, and 0.1, 0.1, and 0.5 percent at 40, 45, and 50 days, respectively. Glucose, fructose, and pentoses were present in varying proportions.

In comparisons [4] between the nitrogen content of lint from live plants and from plants killed by phymatotrichum root rot, higher concentrations were found in the latter in 10 out of 11 sample pairs. The lint from live plants and dead plants averaged, respectively, 0.240 and 0.270 percent nitrogen in 1943 and 0.180 and 0.216 percent in 1944. Higher nitrogen concentrations corresponded with decreased percentages of "mature" fibers and reduced weight-per-inch of fiber.

Methods and Materials

For the determination of total nitrogen, aliquots of the samples were pulled into slivers which were then laid parallel, broken in the middle, and the two halves laid parallel. This breaking and regrouping was continued until the thick bundle of slivers was 3 or 4 inches long. While this bundle was grasped tightly in the middle, 3 sub-samples, each about 0.5 gram in weight, were plucked from the two ends and placed in individual weighing bottles, dried in a draft oven at 78°C for 1 hour, and cooled in a desiccator for final weighing. Large motes and pieces of foreign material were discarded as the sub-samples were drawn.

The acid digestion procedure of Pepkowitz and Shive [9] was followed throughout the investigation. In starting the work, Nessler's reagent was used with a Klett-Summerson photoelectric colorimeter for reading the concentrations. A blank with all reagents and a standard determination were made in connection with each set of 6 to 12 samples run at one time. Within each set, good duplicate agreements were customarily obtained but too frequently another replicate included on a different day was not in good agreement. The colorimetric method was accordingly discarded as unreliable. In its place distillation and titration with sodium hydroxide, using methyl-red indicator, was adopted as the standard procedure. By the latter method agreements between duplicates were usually within 5 percent. The values used for the calculation of the correlation coefficients are either the averages of duplicate determinations by distillation or they are averages of values previously obtained colorimetrically after these had been checked by the distillation procedure.

The methods of measurement of fiber properties and the terms and definitions employed are those in use by the Cotton Branch of the Production and Marketing Administration; these have been reviewed by Webb and Richardson [12].

Grade as assigned by cotton classers has, for purposes of these statistical analyses, been given a numerical rating of 2 for middling fair, 3 for strict good middling, etc., to 10 for good ordinary—that is, increasing numerical values for poorer grades. *Yarn appearance* was measured by comparing panels of the

carded yarns with standard panels. The conventional lettered ratings, A, A −, B +, etc. were converted to numerals, which increase as the appearance becomes poorer.

The statistical methods and criteria of significance noted above are according to Snedecor [11].

Results and Discussion

Maturity and Fineness

Possibly of primary interest, from the theoretical standpoint, is the test of the relationship between total nitrogen-in-lint and the percentage of "mature" fibers. In considering the results (column 9, Table I), it is appropriate to recall that percentages of "mature" fibers are measured as the number per 100 which have wall thicknesses greater than half the diameter of the lumen after the fibers are swollen on a microscope slide in 18-percent sodium hydroxide. By this procedure the wall-lumen relationship is not fully integrated since the fibers are classified as either "mature" or "immature." Furthermore, the swelling method is empirical and may not represent the wall-lumen volume relations at the time of cell death.

All of the upland-cotton nitrogen x maturity correlation coefficients are statistically significant but none of them are very large. Even with the indicated limitation to the interpretation of "maturity" values in mind, these low coefficients would seem to indicate that percentage nitrogen is influenced by factors other than protoplasmic volume relative to fiber weight.

Some evidence of curvilinearity was found when nitrogen content was plotted against maturity, and, as shown in Table I, column 8, the r value for nitrogen x weight-per-inch is higher than that for nitrogen x maturity. On the basis of the 206 upland samples from the Southeast, Midsouth, and Texas and Oklahoma, an r value of -0.62 was obtained when the ratio nitrogen/weight-per-inch was substituted for nitrogen alone. This is substantially better than the nitrogen x maturity value -0.39 from the same sample group and it is also better than the -0.43 found for nitrogen x weight-per-inch, but it does not improve very much the coefficient -0.60 found when maturity was correlated with weight-per-inch.

The correlation coefficients resulting from covariance analyses reported in columns 8 and 9 of Table I reflect the relative influences of heredity and environment on nitrogen x maturity and nitrogen x weight-per-inch relationships. In the upland cottons environment is indicated as being somewhat more important than variety in the nitrogen x maturity relationship but the reverse is indicated in the case of the nitrogen x weight-per-inch relationship. Among the Sea Island cottons opposite effects of heredity and environment are found; in the nitrogen x maturity relationship variety is important and the effect of environment alone is nil, whereas with nitrogen x weight-per-inch it is environmental differences which give the highest coefficients.

Length

The "total" or over-all nitrogen x length correlation coefficients are all low. Marked associations between these properties are developed, however, when environmental and hereditary effects are separated. Varietal differences in length are found to be associated positively with nitrogen, and in upland "varieties" gave a positive value of 0.594 for nitrogen x upper-half mean, whereas strictly environmentally produced changes in length, "within varieties," bear a negative relationship to nitrogen.

In the Sea Island cottons the influences of heredity and environment were outstanding. For upper-half mean length x lint-nitrogen the total coefficient is 0.009. "Varieties," however, give a positive value of 0.416 and "station-years" a negative value of 0.548. The effects of variety and environment thus canceled each other when confounded in a total correlation.

Brown's data [2] have shown that applications of nitrogen, without other fertilizer elements, reduced the length of an upland cotton by $\frac{2}{32}$ inch—that is, more soil nitrogen was associated with shorter length. Nitrogen application would be an environmental effect and, as shown in Table I, negative "within varieties" correlations were obtained. In Sea Island cotton this may also be the case. The Sea Island cottons included a group of 18 samples from an experiment conducted at Gainesville, Florida, in which nitrogen and potash were used separately and in combination as side dressings. The 9 minus-nitrogen length values had an average of 1.63 inches, whereas the 9 plus-nitrogen length values averaged 1.59 inches. The 9 samples from plus-nitrogen plots averaged 0.223 percent nitrogen in the lint and the 9 minus-nitrogen plots gave an almost identical average of 0.220 percent. Eight samples

from plus-potash plots averaged 0.219 percent nitrogen and 10 minus-potash samples averaged 0.223 percent. In neither of these Sea Island examples could the fertilizer effect be construed as important from the standpoint of nitrogen-in-lint. Variety, however, was an important element in this test, which included 5 strains. The strain averages ranged as follows:

Variety	Lint-nitrogen	Upper-quartile mean
12B2	0.190	1.52
Z 8	0.206	1.61
T Z	0.238	1.60
Z 10	0.240	1.63
TZRV	0.242	1.72

The nitrogen x uniformity relationship (Table I, column 7) gave uniformly negative r values, with environmental effects more pronounced than varietal effects. The negative correlations mean that with increasing disparity between mean length and upper-half mean length (lower ratio values) nitrogen increases.

Tensile Strength and X-Ray Angles

In neither the upland nor the Sea Island cottons is there evidence of significant relationships between nitrogen-in-lint and either fiber strength (Table I, column 10) or x-ray angles (column 11). It may be noted, nevertheless, that in the upland cotton environmental coefficients for nitrogen x fiber strength are characterized by negative signs, whereas in Sea Island ones the opposite effect is obtained.

Yarn Properties

Positive and statistically significant "total" correlation coefficients are found for both the upland and Sea Island cottons between nitrogen-in-lint and both skein strength (Table I, column 12) and yarn appearance (column 13). The segregation of varietal effects improved the yarn strength correlations in the upland cottons, whereas it was the segregation of the environmental effects which improved the Sea Island coefficients. With respect to yarn appearance the varietal segregations improved both the upland and Sea Island coefficients.

One of the highest correlation coefficients appearing in Table I is the "varieties" value 0.685 found between nitrogen-in-lint and yarn strength in upland cotton. Such a coefficient is in good keeping with the "varieties" values 0.594 for nitrogen x upper-half mean length and -0.648 for nitrogen x weight-per-inch—that is, long, fine cottons produce the strongest yarns.

Inasmuch as the numerical rating of yarn appearance increases as appearance becomes poorer, the uniformly positive nitrogen x appearance correlation coefficients support the generally recognized relationship that finer fibers produce rougher yarns.

Picker and Card Waste

In the upland cottons varieties with much picker and card waste tended to have little nitrogen, but environmental effects (within varieties) that increased waste tended also to increase nitrogen. In the Sea Island cottons all correlation coefficients between nitrogen and amount of waste are positive and all are relatively high.

Results of a Drought and Fruitfulness Experiment

In an experiment conducted in 1945 at College Station, Texas, measurements were made of the effects of drought and fruitfulness on the fiber properties of five varieties of cotton. The experiment included comparisons between plants in both irrigated and nonirrigated plots that had normal numbers of bolls and plants reduced to two bolls per plant by the removal of squares and flowers. Both treatments influenced plant growth significantly but there were a number of rains during the summer and the plants in the nonirrigated plots wilted only occasionally. A factorial summary of the effects of the treatments on nitrogen-in-lint, upper-half mean length, and fineness of fiber, together with correlation coefficients, are reported in Table II.

Analyses of variance (not reported in Table II) show a highly significant increase in lint-nitrogen as a result of drought and a decrease as a result of reducing fruiting to two bolls per plant, but between varieties the differences were not significant. Differences between pickings were highly significant for each of the three properties.

The correlation coefficients derived from the data of this experiment follow the trends established in Table I—that is, varietal effects had a much greater influence on nitrogen x length than did treatments, whereas treatments had greater influence on nitrogen x fineness. As in the "total" correlations of Table I, variations in nitrogen were associated in a positive

TABLE II. FACTORIAL SUMMARY AND CORRELATION COEFFICIENTS OF NITROGEN-IN-LINT, UPPER-HALF MEAN LENGTH AND WEIGHT-PER-INCH OF THREE COTTON PICKINGS IN A 1945 EXPERIMENT AT COLLEGE STATION, TEXAS

Treatment	Nitrogen-in-lint				Upper-half mean length				Weight-per-inch			
	1st	2nd	3rd	Mean	1st	2nd	3rd	Mean	1st	2nd	3rd	Mean
Factorial summary												
Wet (irrigated)	0.173	0.136	0.129	0.146	1.06	1.02	1.04	1.04	4.7	4.7	4.7	4.7
Dry (nonirrigated)	0.197	0.163	0.156	0.172	1.04	0.98	0.91	0.97	4.3	4.6	4.8	4.5
Fully fruited	0.192	0.160	0.145	0.166	1.03	0.99	0.99	1.00	4.4	4.6	4.7	4.5
2 bolls per plant	0.179	0.140	0.139	0.152	1.06	1.01	1.03	1.03	4.7	4.8	4.8	4.7
Stoneville 2-B	0.183	0.155	0.157	0.165	1.12	1.07	1.09	1.09	4.0	4.2	4.0	4.0
Ark. Rowden	0.182	0.153	0.143	0.159	1.08	1.05	1.05	1.06	4.3	4.5	4.5	4.4
Okla. Tri. 92–1–1	0.197	0.152	0.159	0.169	1.05	1.01	1.02	1.02	4.4	4.6	4.5	4.5
D. & P. L.	0.184	0.146	0.125	0.152	1.11	1.07	1.06	1.08	4.4	4.6	4.6	4.5
Hibred	0.179	0.142	0.128	0.149	0.88	0.81	0.82	0.83	5.6	5.6	6.1	5.7
Means	0.186	0.150	0.143	0.160	1.05	1.00	1.01	1.02	4.54	4.70	4.74	4.62

Correlation coefficients	No. of samples*	Upper-half mean length	Weight-per-inch
Nitrogen-in-lint with:			
Total	60	0.176	−0.402**
Varieties	5	0.503	−0.679
Treatments	12	0.083	−0.741**
Within treatments	48	0.237	−0.466**
Within varieties	55	0.137	−0.579**

* Degrees of freedom = n − 2, or 58, 3, 10, 46, and 53 for total, varieties, treatments, within treatments, and within varieties, respectively. ** Statistically significant by odds of 99:1.

direction with length variation but negatively with weight-per-inch variations.

Nitrogen-in-Lint Versus Nitrogen and Carbohydrates in the Plant

An opportunity for correlating nitrogen-in-lint with nitrogen and carbohydrates in the plant is provided by data from an experiment with Acala P18-c conducted at Shafter, California, during 1946. Six treatments were applied to plants growing both in an irrigated block and in a very dry, nonirrigated block. The six treatments, as reported by numbers in Table III, were as follows: (1) no treatment (control plants); (2) flowers removed, leaving only two bolls to develop; (3) all branches removed, in bud stage, from main stalks except for two fruiting branches with only one node, from each of which a boll was developed—that is, plants with two bolls; (4) same as (3) except that the terminal bud was removed soon after the second boll was set; (5) one-half of each leaf cut away weekly; (6) shaded with muslin shades that reduced the light intensity at the tops of the plants to 25 percent of full exposure.

All treatments were started at the time of first flowers, or before, but the experiment was duplicated with plants whose bolls were from (*a*) flowers appearing between June 25 and July 4, and (*b*) later ones appearing between July 12 and 26.

Plant samples for carbohydrate and nitrogen determinations were collected during two periods. These samples were of (*a*) medium-age main-stalk leaves, (*b*) middle third of main stalks, and (*c*) large roots as lifted with a shovel. Each sample consisted of 12 plants, 3 plants being taken respectively in the mid-mornings and mid-afternoons of two successive days. The first set of samples was collected on July 16 and 17 and the second set on August 6 and 7. These dates of sampling correspond approximately with the early period of secondary thickening of the fibers of the respective series of bolls.

Nitrogen-in-lint from the dry plants (Table III) averaged 50 percent higher than in the lint from the frequently irrigated plants. Differences in favor of the dry plants were consistent throughout the data. Consistent also were the large increase in the lint-nitrogen of half-leaf plants (treatment 5) and the decrease in the lint-nitrogen of the shaded plants (treatment 6). The treatments resulted in some substantial, but usually lesser, changes in the nitrogen and carbohydrate concentrations in the plant tissues.

* Statistically significant by odds of 19 to 1. ** Statistically significant by odds of 99 to 1.

TABLE I. MEAN FIBER AND YARN PROPERTIES AND SIMPLE CORRELATION COEFFICIENTS BY COVARIANCE OF NITROGEN WITH THESE PROPERTIES

Column →	(1)	(2)	(3)	(4)	(5)	Length (6)	(7)	(8)	(9)	(10)	(11)	22s Yarn (12)	(13)	(14)
	Samples (number)	Nitrogen-in-lint (%)	Grade	Staple length (32nd's inch)	Mean (in.)	Upper-half mean (in.)	Uniformity ratio	Weight-per-inch (mg.)	Mature fibers (%)	Fiber tensile strength (1,000 lb./sq. in.)	X-ray angles (degrees)	Skein strength (lb.)	Appearance (grade)	Picker and card waste (%)
Mean fiber and yarn properties														
Upland cottons	158	0.188	—	32	0.75	0.98	76.3	4.48	74.5	78.0	33.8	97.5	3.9	7.5
Sea Island	49	0.231	6	48	—	1.62[1]	—	2.8	74.2	100.0	—	52.0[2]	6.2[2]	14.9
Simple correlation coefficients														
Upland cottons														
Total	158	—	—	0.209**	0.101	0.249**	−0.281**	−0.493**	−0.376**	0.038	0.023	0.329**	0.301**	0.140
Varieties[3]	49	—	—	0.579**	0.430**	0.594**	−0.248	−0.648**	−0.302*	0.232	0.055	0.685**	0.525**	−0.258
Station-years[4]	53	—	—	0.176	0.052	0.242	−0.338*	−0.556**	−0.431**	−0.043	0.082	0.312*	0.448**	0.195
Within station-years[5]	105	—	—	0.259**	0.183	0.261**	−0.178	−0.396**	−0.273**	0.184	0.060	0.358**	0.105	−0.013
Within varieties[6]	109	—	—	−0.166	−0.160	−0.152	−0.337**	−0.371**	−0.447**	−0.143	0.098	−0.062	0.121	0.412**
Sea Island														
Total	49	—	0.392**	−0.241	—	0.009[1]	—	−0.451**	−0.158	0.281	—	0.294*	0.309*	0.618**
Varieties[3]	10	—	0.418	0.363	—	0.416	—	−0.427	−0.249	−0.168	—	0.232	0.415	0.779**
Station-years[4]	7	—	0.516	−0.728*	—	−0.548	—	−0.669	0.029	0.352	—	0.437	0.297	0.634**
Within station-years[5]	42	—	0.214	0.258	—	0.340**	—	−0.357*	−0.246	−0.172	—	0.103	0.365*	0.648**
Within varieties[6]	39	—	0.419*	−0.536**	—	−0.501**	—	−0.529**	−0.056	0.290	—	0.340*	0.098	0.454**

[1] Upper-quartile mean. [2] 60s yarn. [3] Principally variety but confounded with environmental effects. [4] Principally environment but confounded with varietal effects. [5] Varietal effects freed from environment. [6] Environmental effects freed from variety. * Statistically significant by odds of 19 to 1. ** Statistically significant by odds of 99 to 1.

TABLE III. FACTORIAL SUMMARY AND CORRELATION COEFFICIENTS OF NITROGEN-IN-LINT WITH NITROGEN AND CARBOHYDRATES IN PLANTS, SHAFTER, CALIFORNIA, 1946 (PERCENTAGE ON DRY WEIGHTS)

Treatment	Nitrogen-in-lint	Nitrogen in plants: Soluble Leaves	Soluble Stems	Soluble Roots	Insoluble Leaves	Insoluble Stems	Insoluble Roots	Carbohydrates in plants: Total sugars Leaves	Total sugars Stems	Total sugars Roots	Starch Leaves	Starch Stems	Starch Roots
Factorial summary													
Wet (irrigated)	0.198	0.62	0.55	0.31	2.95	0.60	0.51	1.23	3.27	3.13	2.41	1.64	4.01
Dry (nonirrigated)	0.298	0.73	0.67	0.31	2.36	0.54	0.44	1.02	5.00	4.97	1.60	3.35	7.90
1 (control)	0.238	0.71	0.39	0.26	2.48	0.47	0.44	0.81	5.55	4.95	1.49	2.19	4.67
2 (2-boll)	0.254	0.62	0.38	0.29	2.62	0.57	0.38	1.13	5.13	4.38	2.07	3.52	6.81
3 (no branches)	0.239	0.72	0.74	0.42	2.85	0.69	0.49	0.95	3.51	3.40	2.32	2.11	7.43
4 (same less bud)	0.239	0.69	1.01	0.45	2.34	0.65	0.64	1.45	1.89	3.82	2.43	4.77	11.16
5 (half-leaf)	0.290	0.69	0.54	0.24	2.48	0.50	0.49	1.04	4.83	4.32	1.99	1.54	3.53
6 (shade)	0.217	0.61	0.35	0.21	2.55	0.52	0.43	1.18	4.44	3.86	1.81	0.85	2.37
Correlation coefficients													
Nitrogen-in-lint with:		0.614**	0.119	−0.093	−0.545**	−0.237	−0.161	−0.314	0.469*	0.611**	−0.466*	0.256	0.374

* Statistically significant by odds of 19 to 1. ** Statistically significant by odds of 99 to 1.

Deficient soil moisture with associated reductions in tissue moisture resulted in an 18 percent increase in lint-nitrogen in an experiment in which little wilting occurred. In another experiment during which the wilting was severe and prolonged the nonirrigated cotton had 50 percent more lint-nitrogen than did the irrigated cotton.

In the latter experiment soluble nitrogen in leaves x total nitrogen-in-lint gave a positive coefficient of 0.61. Insoluble nitrogen in leaves x lint-nitrogen, on the other hand, gave a negative 0.55. Total sugars in leaves x total nitrogen-in-lint gave an r value of -0.47, whereas total sugars in the middle third of the main-stalk x lint-nitrogen gave a positive 0.26.

Acknowledgments

The writer is indebted to Howard E. Joham and Sue B. Krug for the chemical determinations and to the latter and to Virginia M. Kuykendall for assistance with the statistical analyses. Special acknowledgment is due to Dr. Henry D. Barker, who suggested the use and outlined the application of the covariance analyses.

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Pairing the corresponding values throughout the first and second series, a relatively good positive correlation coefficient of 0.614 is found between nitrogen-in-lint and the soluble nitrogen in leaves. The r value for nitrogen-in-lint x nitrogen in the stems is smaller but positive and that for the roots becomes negative.

A negative correlation coefficient, -0.545, is found between nitrogen-in-lint and the water-insoluble nitrogen in leaves. Lower coefficients are found with insoluble nitrogen in stems and roots. Although causal relationships are not necessarily indicated by significant correlation coefficients, the results suggest that conditions which promoted the formation of proteins or other nonlabile nitrogenous substances in the leaves reduced labile nitrogen and thereby the nitrogen supply available for translocation to bolls. As evidence that this may be the correct interpretation, a highly significant correlation coefficient of -0.499 is found between soluble and insoluble nitrogen in the leaves.

For the correlations between the total-sugars and x lint-nitrogen, a negative coefficient, -0.314, is found with leaf sugars; a positive, 0.469, with stem sugars, and a positive, 0.611, with root sugars. This set of relationships could mean, when taken in conjunction with the leaf nitrogen, that with less of the leaf sugar going into protein formation a greater supply of labile nitrogen remains available for translocation to bolls. This suggestion probably represents an over-simplification; that there is something more complex than this involved is indicated by the fact that the nitrogen and carbohydrate levels in the plant tissues of treatment 5 (half-leaf) are much like those of treatment 6 (shade) and yet the lint of the former contained much more nitrogen than the lint of the latter.

Summary and Conclusions

Employing simple correlation coefficients, comparisons were made between variations in the total nitrogen content of cotton fibers and variations in the physical properties of these fibers and their yarns. The samples were selected at random from regional samples stocks of several crop years. For these comparisons nitrogen determinations were made on 248 upland and 66 Sea Island cottons. Results from additional measurements on samples from experimental plots support the conclusions drawn from the random samples. Covariance analyses have shown that in some instances hereditary and environmental factors have opposite influences on nitrogen x fiber-property relationships.

Among the upland cottons some of the more outstanding correlation coefficients, broken down for varietal and environmental effects, were found to be as follows: lint-nitrogen x staple length gave 0.58 for varieties and 0.18 for station-years; lint-nitrogen x weight-per-inch gave -0.65 for varieties and -0.56 for station-years; nitrogen x percentage of mature fibers gave -0.30 for varieties and -0.43 for station-years; nitrogen x skein strength of 22s carded yarn gave 0.68 for varieties and 0.31 for station-years; nitrogen x appearance of 22s yarn gave 0.52 for varieties and 0.45 for station-years (as yarn appearance becomes poorer its numerical rating increases); nitrogen x picker and card waste gave -0.26 for varieties and 0.19 for station-years. As further illustrations of the sometimes counteracting effects of variety and environmental influences on total or over-all correlations, no relationship was found in Sea Island between nitrogen and fiber length, but within station-years the r value was a highly significant positive 0.34, whereas for within varieties the value became a negative 0.50.

Using a number of relatively inexpensive measurements of fiber properties in multiple correlations wherein varietal and environmental influences were separately evaluated, Barker [1] has developed equations whereby the strength and appearance of yarns can be forecast with creditable accuracy. It remains for later determinations to indicate whether the introduction of lint-nitrogen into such equations would bring out points of practicable applicability. Likewise the present data are not very well suited to the development of the significance of lint-nitrogen in other directions.

It is possible that the level of nitrogen in the cotton fibers, here measured as of the time of cell death, bears a causal relationship with those physical properties of fibers with which it has been found to be correlated. As an alternate view, the variations in lint-nitrogen and associated variations in physical properties could be regarded as simultaneous but independent responses to antecedent chemical and physical conditions within the tissues of the plant which supported the growth of the fibers. Data bearing on relationships between lint-nitrogen and nitrogen, carbohydrate, and moisture levels in the plant are provided from two field experiments.

Book Reviews

Definition and Measurement of Gloss. A Survey of Published Literature. V. G. W. Harrison. London, Printing and Allied Trades Research Association, 1945. 145 + vi pages. Price, 10 shillings.

(Reviewed by Earl K. Fischer, Institute of Textile Technology, Charlottesville, Virginia)

This small volume fills a definite need. The objective of the author was to present a critique of published papers covering the whole subject of gloss from both the physical and psychological viewpoints. There are 180 references which include various types of contributions from very early work to papers as recent as 1945. The survey appears quite complete, although some omissions have been noted. A few patents have been included.

The book is organized in four sections: the first deals with the physical factors which lead to the sensation of gloss or luster; the second describes physiological and psychological factors; the third is concerned with the design of instruments and practical measuring procedures; and the last section includes a discussion of the present state of knowledge on the subject and outlines new avenues for research with reference, particularly, to the plans of the PATRA laboratories. A uniformly critical tone is maintained and the reader gains the impression that the material has been sifted and studied, an impression strengthened by the informal, first-person style.

Reflection of light from different surfaces is far from a simple matter. The author's analysis starts from plane, mirror-like surfaces, and proceeds finally to light-scattering surfaces containing many small reflecting and refracting units. Most surfaces are neither ideally matte nor perfect mirrors. Consequently, any instrument which supplies a single-point reading of specularly reflected light and fails to account for light reflected at other angles is of little value; nevertheless, such instruments have been widely used, although they never prove satisfactory. Instruments which measure reflectance at two or more positions are of greater usefulness and permit the computation of gloss-index ratios. Only a complete survey of reflectance at all angles, as provided by a goniophotometer, can supply data for a complete specification of the optical properties of any surface. Such data are illustrated throughout the book exclusively by intensity-distribution curves plotted on polar coordinates. No satisfactory system of gloss designation has been devised so far although various methods have been used and some have acquired the authority of sponsorship by industry standard associations.

Gloss is the interpretation of a sensation. The human eye is a remarkably sensitive photometer, but the record of its observations is subject to innumerable influences, among them emotion, prior experience, fatigue, etc. Physical measuring instruments, on the other hand, depend on far less sensitive and adaptable elements than the eye, but the data have an objective quality. The author has made an effort to interpret experimental data in terms of visual equivalents, and the extraordinary difficulty of such an undertaking is evident, leading to the dilemma that "if we try to analyze gloss or luster into physical properties of a surface, we may in the process of analysis lose the very thing for which we are looking." This effort at understanding is both desirable and necessary, for the physicist is inclined to give little attention to the subjective factors in gloss measurement.

Examples are scattered throughout the book, and of these one is of special interest in textile design: black-and-white striped goods, with the black predominating, often appear lustrous although the cloth itself is not glossy. This illusion has numerous counterparts, and the conclusion is that one characteristic of this kind of gloss is visual confusion or indeterminacy.

As a background for research on gloss measurement this book will prove of great value. It will be equally useful to those concerned with practical measurements, if only to show the limitations of methods currently in use. Dr. Harrison is to be congratulated for this skillful survey of a difficult and confusing subject.

Action of Alkali upon Cellulose. Albert Schaeffer. Office of the Publication Board, U. S. Department of Commerce, 1947. Textile Series, Report No. 33.*

(Reviewed by Eugene Pacsu, The Textile Foundation and Princeton University)

This research report was prepared in the Textile Application Laboratory, I. G. Farben, Höchst, and translated at the request of the Textile Team of the Research and Development Branch, Office of The Quartermaster General.

In the experiments described the degree to which the cellulosic fiber is damaged by the action of different alkalies in boiling baths depends upon the kind of fiber and the nature and concentration of the alkali. It was found that in the boiling treatment in the presence of alkali it was the oxygen dissolved in the bath which, to a large extent, caused the increase in damage factor and the decrease in tensile strength of the cellulosic fibers. Unusually strong fiber decomposition in some experiments is explained as being due to salts (copper) which act as oxygen carriers. Possible mechanism of oxidative degradation postulates the hydrolytic splitting of a glucopyranose ring, followed by oxidation of the product obtained to the ester cellulose, and saponification of the ester group. Fiber damage caused by alkaline boils is minimized by the addition of magnesium trisilicate to the boiling and rinsing baths, by rinsing until neutral, and drying below 100°C.

Organic Chemistry. Paul Karrer. Second English edition, translated by A. J. Mee, with assistance on recent additions and revisions by M. F. Darken. New York, Elsevier Publishing Co., Inc., 1946. 953 + xx pages. Price, $7.50.

(Reviewed by William P. Utermohlen, Jr., Institute of Textile Technology, Charlottesville, Virginia)

Dr. Karrer's outstanding volume on organic chemistry has been revised and enlarged in this second English edition, and is priced very reasonably for a book of its quality and scope. It appears to have more of the desirable qualities of a one-volume textbook for advanced college students than any other book in English, although it is definitely lacking in some of the features found in the best-known organic textbooks authored in America.

Karrer's work is particularly valuable in the field of naturally occurring organic compounds. Thus, pyrones and quinones, terpenes and other alicyclic compounds, heterocyclic compounds, and alkaloids receive unusually complete treatment. The entire book is especially strong in the fields of synthesis and in proof of the constitution of organic compounds. Its typography and representation of structural formulas are excellent. The subject matter is presented in quite a readable manner except where misleading words and awkward sentence structure occur. These are probably inevitable results of translation from the German original.

In general, this book represents the classical, largely descriptive organic chemistry of continental Europe, and gives little attention to the physical-organic chemistry, mechanisms of reactions, and other theoretical developments of the modern English and American schools. However, in the presentation of a very large body of information, much of which has been brought up to date by this revision, and in making organic chemistry seem real and alive, this book appears to be the best general text on organic chemistry available.

Bulletin of the National Association of Wool Manufacturers. Volume 76. Published by the Association, 386 Fourth Ave., New York; 80 Federal St., Boston. 525 pages. Price, $10.00.

The 1946 *Bulletin* of the National Association of Wool Manufacturers is divided into three parts. Part I deals with matters pertaining to the Association, such as by-laws, list of members, and a 41-page secretary's report of various activities of the Association. Part II, 278 pages, furnishes, as usual, comparative statistics for a period of several years relating to the wool textile industry. It includes raw materials; amount, activity, and location of machinery; number and size of establishments; labor and products; imports and exports; and data on finance and operation.

Part III, 161 pages, is of special interest because it presents briefs and statements by the Association and by various prominent manufacturers representing

* A limited number of copies are available free at the Textile Section, Military Planning Division, Office of The Quartermaster General, Washington, D. C.

the Association in support of the Association's stand on reciprocal trade agreements and on tariff. Arthur Besse, president of the Association, discusses also the proposed charter for an International Trade Organization. A chapter is devoted to tables showing changes in United States import duties on wool and wool manufacturers since the Tariff Act of 1930. A chapter deals with the wage structure in the woolen and worsted industry, and in another chapter wool production costs are discussed.

The German Cotton, Rayon, and Silk Industries. D. W. Hill and Associates. Brooklyn, Mapleton House, 1947. 156 pages. Price, $5.00.

This is a report of the British Intelligence Objectives Sub-Committee. The original is on file in Washington under the Office of Technical Services, number PB 34729. It presents a survey of the German cotton, rayon, and silk industries. The book is issued in a handy pocket-size edition. It is printed by the photo-offset process in readable type, and the charts and tables are legible.

The chief objective of the survey was to obtain information on the processing of fibers, yarns, and fabrics rather than on the production of fibers such as rayon. Particular attention was given to the investigation of new developments in the fields of spinning, weaving, printing, dyeing, and finishing.

Development of Mersol and Hostapon Processes. W. Baird. Brooklyn, Mapleton House, 1947. 41 pages. Price, $3.00.

This report by a British Team is on file in Washington, as report PB 31278, of the Office of Technical Services. Like the report, by the same publishing house, on German processing developments, also reviewed in this issue, it is a photo-offset reproduction. In this case the print is legible, but very fine. It is profusely illustrated with flow sheets and tables. Some of the former have had so much photographic reduction that they are not completely legible.

The text consists of I. G. Farben reports, in translation, dealing with the development work on the Reed reaction to produce Mersol H and on a new reaction to give alkylsulfonic acids by catalyzed reaction of paraffins with sulfur dioxide and oxygen.

ABSTRACTS

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A list of periodicals, the abbreviations used in references to articles, and the addresses of publishers of English language publications is given on page 37 of the January, 1947, issue.

ANALYSIS: TESTING: LABORATORY METHODS

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Carboxyl Determination in Cellulose

Carboxyl determination in the cellulose of cotton and in technical pulp. O. H. Weber. *Textil-Rundschau* **2**, 117–23 (1947) (through *Chem. Abstr.* **41**, 5305*b* (Aug. 20, 1947)).

A method is described in detail for carboxyl determination as an aid in ascertaining the degree to which the fibers of technical lignocellulose are dissimilar. This is based on the author's "reversible-methylene blue method" (*C.A.* **36**, 653[5]).

Text. Research J. Oct. 1947

Molecular Weight of Cellulose

Recent ultracentrifugal investigations on cellulose and cellulose derivatives. Ingvar Julliander. *J. Polymer Sci.* **2**, 329–45 (June 1947).

A review of the theory of determining molecular weights and molecular weight distributions of cellulose and cellulose derivatives from sedimentation and diffusion data. The question of what type of average molecular weight is obtained is discussed in detail. Data on several samples of nitrocellulose are given. E. D. Klug

Text. Research J. Oct. 1947

Microscopy

On a method of increasing contrast in microscopy. T. Merton. *Proc. Roy. Soc.* **A189**, 309–13 (May 1, 1947).

A description is given of the mounting of specimens between half-silvered glass plates having about 50% transmission, whereby interference phenomena are produced and the objects appear colored against a contrasting background. A method of platinizing glass, which gives a more durable coating than silvering, was developed. It was found possible to transfer the thin layer of platinum from the glass to cellulose acetate foil. A sample consisting of small particles could then be mounted on platinized glass and covered with the platinized foil, when interference fringes appeared around each particle, the number of fringes depending on particle size. It is estimated that particles down to 100 mμ can be measured by this method, and with some refinements particles as small as 10 mμ might be detected.

Text. Research J. Oct. 1947 W. E. Davis

Molecular Weight Determination

The determination of molecular weight by light-scattering. W. H. Markwood, Jr. *J. Franklin Inst.* **244**, 92–4 (July 1947).

This is an account of a seminar on the above subject, which provides a brief review of the equations applicable to light-scattering by solutions of molecules which are small in relation to the wave length of light, as well as the corrections to be applied for larger molecules of various shapes. W. E. Davis

Text. Research J. Oct. 1947

Structure of Polyamides

The crystal structure of two polyamides (nylons). C. W. Bunn and E. V. Garner. *Proc. Roy. Soc.* **A189**, 39–68 (Mar. 27, 1947).

Fibers and sheets of both 6–6 and 6–10 polyamides were examined by x-ray and optical methods. Both have analogous structures, built up of parallel sheets of linear molecules. The sheets occur in two arrangements, giving an alpha and a beta form for each of the polyamides; mixed arrangements also exist. Some analogies with the structure of the fibrous proteins are pointed out. W. E. Davis

Text. Research J. Oct. 1947

Ash in Viscose

A physicochemical study of cellulose, viscose, and fibers. I. Eduardo Blanchard Castillo. *Anales fís. y quím.* (Madrid) **42**, 1019–35 (1946) (through *Chem. Abstr.* **41**, 5303*i* (Aug. 20, 1947)).

The Hermans and Bredee filtration index (*C.A.* **29**, 6801[6]), $C_f/2t = t/P - 1/v_0$, where C_f is the filtration index, v_0 the initial velocity of filtration, t the time, and P the quantity filtered, is introduced as one of the criteria of viscose cellulose from straw. Prehydrolysis by H_2SO_4 gives a harsher product, whereas the action of SO_2 gives a softer or bland product. A greater concentration of α-cellulose in the original product is a guarantee of better filtration. The Cu number and degree of polymerization of cellulose have no apparent influence on filtration. Ash is a factor playing a great role in filtration; when reduced by prehydrolysis or other means, filtration improves. Straw cellulose is high in ash, which can be reduced considerably by prehydrolysis. 5 references.

Text. Research J. Oct. 1947

CHEMICAL AND PHYSICAL RESEARCH

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Cellulose Acetate Phthalates

Reactions of tetrachlorophthalic anhydride with cellulose derivatives. William P. Utermohlen, Jr., and E. Louise Wallace. *J. Polymer Sci.* **2**, 275–80 (June 1947).

Attempts were made to esterify cellulose acetate (substitution 2.0) and ethyl cellulose (substitution 2.25) with tetrachlorophthalic anhydride. In the presence of pyridine, a reaction between the pyridine and the anhydride occurred. In dioxan at 100°C, products of substitution 0.14 and 0.23 were obtained with cellulose acetate and 0.29 with ethyl cellulose. Under similar conditions, phthalic anhydride gave a substitution of 0.83 and 0.52 respectively in pyridine, and 0.39 and 0.29 in dioxan. The tetrachlorophthalate of cellulose acetate was soluble in 5% NaOH, acetone, and dioxan. The corresponding derivative of ethyl cellulose was soluble in organic solvents and 5% NH_4OH but insoluble in dilute NaOH. E. D. Klug

Text. Research J. Oct. 1947

Solubility of Gases in Elastomers

Solubility, diffusion, and permeation of gases in gutta-percha. G. J. Van Amerongen. *J. Polymer Sci.* **2**, 381–6 (Aug. 1947).

The permeability of vulcanized gutta-percha membranes to gases was determined in relation to the rate of diffusion and solubility. The measurements, as functions of temperature, with 4 gases were taken below and above the melting point of gutta-percha. The evidence is that the rates of permeation and diffusion increase sharply at approximately 45°C, owing to melting of the gutta-percha. In the same way, although to a lesser degree, the solubility of the gas likewise increases at the melting point. The activation energies of permeation and diffusion with the heat of solution were computed from the temperature function of those quantities. It follows from the results that crystallization of the elastomer reduces the gas-solubility, the diffusivity, and the permeability, and increases the activation energy of diffusion. The interpretation of this high activation energy of diffusion is that, because of the crystallization, the macromolecules of the membrane adhere so firmly that greater energy is required to admit the gas molecules. Author

Text. Research J. Oct. 1947

Molecular Friction Coefficient

Effect of centrifugal field on resistance to motion of threadlike molecules in solution. Seymour J. Singer. *J. Polymer Sci.* **2**, 290–5 (June 1947).

It is calculated that the effect of a centrifugal field on the frictional coefficient of a threadlike molecule corresponding to the model of Kuhn and Kuhn is negligible.

Text. Research J. Oct. 1947 E. D. Klug

Heat Conduction and Molecular Structure

Heat conduction and molecular structure in rubber-like polymers. John Rehner, Jr. *J. Polymer Sci.* **2**, 263–74 (June 1947).

The thermal diffusivity of gum stocks prepared with natural rubber, butyl (GR-I), Perbunans 18, 26, and 35, Buna S, polybutadiene, Neoprene GN, polyisoprene, and Silastic 160 and 180, with and without hydrocarbon softener, and carbon black was determined.

Text. Research J. Oct. 1947 E. D. Klug

X-Ray Photographs of Fibers

A study of some vegetable fibers by x-ray diffraction method. C. R. Bose and N. Ahmad. *Indian J. Phys.* **20**, 105–10 (1946) (through *Chem. Abstr.* **41**, 4916*c* (Aug. 10, 1947)).

X-ray photographs of several kinds of clean, delignified, and fat-free cellulosic fibers were taken and their tensile strengths measured. The fibers showing extensions of the spots along the Debye-Scherrer rings indicating disheveling of the fiber molecules were found to have tensile strengths generally smaller than those of other fibers. The fibers of *Agava sisalana* (sisal hemp) and *Sansevieria roxburgiana* gave ring-shaped photographs showing that the distribution of micelles in them was chaotic and at random. Diffraction patterns of these 2 kinds of fibers in a stretched condition showed that stretching partially orients the micelles in a direction parallel to the length of the fiber.

Text. Research J. Oct. 1947

Internal Plasticization

Internal plasticization: The effect of chemical structure. V. L. Simril. *J. Polymer Sci.* **2**, 142–56 (Apr. 1947).

The elastic and plastic properties of high polymeric materials are functions of the forces holding the

molecules together and the ability of small segments of the chains to move about, relative to other segments. Internal plasticization is accomplished by introducing structural features which reduce intermolecular and intramolecular forces and which, in general, decrease the order of the polymer. Physical techniques used to determine the effect of such structural features are discussed. The results of numerous investigations into the relations between structure and properties have been considered in an attempt to present a simple and consistent physical picture of these relations.

Text. Research J. Oct. 1947 Author

Diffusion of Water into a Polymer

Diffusion of water into a polymer. J. F. H. Custers. *J. Polymer Sci.* **2**, 301–5 (June 1947).

In contradistinction to the usual methods, the diffusion of water into a polymer has been investigated by starting from a disc of the material surrounded by water. In this way, actual service conditions are often closely approached. Since a theoretical basis is desirable, equations are given for this type of diffusion, and experiments with a wood flour containing phenol-formaldehyde material were performed from which values for the permeation constant could be derived.

Text. Research J. Oct. 1947 Author

Melamine Resins

Melamine resins—their chemistry, preparation, and characteristics. R. W. Moncrief. *Paint Manuf.* **17**, 149–53 (1947) (through *Chem. Abstr.* **41**, 4951*h* (Aug. 10, 1947)).

The chemistry and methods of preparation of melamine are explained, and the reaction of melamine with CH_2O, and of the conversion of methylolmelamines to resins. The alkylated methylolmelamines are soluble in water yet convertible by the action of heat and catalysts into infusible insoluble resins. Interesting possibilities exist for the industrial utilization of colloidal solutions of melamine-CH_2O resins, which, when suitably prepared, exhibit the property of cataphoresis.

Text. Research J. Oct. 1947

BLEACHING: DYEING: FINISHING

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Bleaching and Dyeing

A scientific outlook on dyeing, bleaching, and mercerizing practice. P. M. Joshi. *Indian Text. J.* **56**, 824–31 (June 1946).

Practical suggestions are given for controls in dyehouse practices with respect to supplies of dyes, chemicals, and auxiliaries; for examination of goods prior to processing to determine amount and nature of size, width of gray cloth, mechanical defects, and nature of dyes used in colored goods; and for tests after bleaching for strength, removal of size, and tendency of bleached cloth to become brownish on storing. Some details of dyeing and mercerizing processes are discussed.

Text. Research J. Oct. 1947 R. K. Worner

Glue in Dyeing

Glue in dye bath. V. D. Riswadkar. *Indian Text. J.* **57**, 253–4 (Dec. 1946).

Glue is a good retarding and leveling agent when used in vat-dyeing cotton yarns. R. K. Worner

Text. Research J. Oct. 1947

Wool-Dyeing Cellulose

Increasing the affinity of cellulose for wool dyes. Renaud. *Ind. textile* **62**, 56–7 (1945); *Chimie & industrie* **56**, 130 (1946) (through *Chem. Abstr.* **41**, 5310*g* (Aug. 20, 1947)).

Natural or reprecipitated cellulose fibers can be rendered capable of fixing wool dyes by incorporating into the fibers certain N compounds consisting of high-molecular-weight condensation products obtained by reaction of compounds containing at least 2 radicals capable of yielding esters or amides, the compounds being selected so that the condensation products will contain basic radicals. Various types of suitable condensation products are listed. On the whole, the shades thus obtained are not as fast as the corresponding shades on wool.

Text. Research J. Oct. 1947

Diffusion of Dyes

Anisotropic diffusion of direct dyes in fibers. A. Frey-Wyssling. *J. Polymer Sci.* **2**, 314–17 (June 1947).

Diffusion of Congo red in water or 50% glycerol through viscose fibers embedded in Canada balsam occurred only perpendicular to but not parallel to the fiber axis. A mechanism whereby diffusion through the crystalline lattice takes place is suggested. E. D. Klug

Text. Research J. Oct. 1947

Lignocellulose

The acid nature of vegetable fibres in relation to basic dye absorption. P. B. Sarkar, H. Chatterjee, A. K. Mazumdar, and K. B. Pal. *J. Soc. Dyers and Colourists* **63**, 229–31 (July 1947).

Twelve vegetable fibers have been analyzed for their lignin, carbon dioxide, furfural, holocellulose, etc., contents. Their acid values and absorption of methylene blue have been measured; there exists a fairly close relationship between these two values. It is suggested that the absorption of basic dyes by these lignocelluloses is due to the presence of acidic constituents of the hemicelluloses, rather than to lignin. The existence of an ester linkage between the hydroxyl group of lignin and the carboxyl group of polyuronic acid is postulated for 9 fibers which, unlike the others, yield an appreciably higher percentage of carbon dioxide and furfural. Authors

Text. Research J. Oct. 1947

Dye Penetration and Shade

Penetration means less depth of shade. Narhari H. Shah. *Indian Text. J.* **57**, 458, 460 (Feb. 1947).

When mercerized and unmercerized goods are dyed under the same conditions, the former is much darker in color owing to differences in optical properties and to reduced penetration of the dyes. It takes up relatively little more dye than the unmercerized. Under the same conditions, rayon takes on a much darker shade than unmercerized cotton because of a combination of three factors—namely, additional color absorbed, differences in reflectance between cotton and rayon, and difference in penetration.

Text. Research J. Oct. 1947 R. K. Worner

Antishrink Process

New antishrink process. F. C. Wood. *Textile Colorist and Converter* **67**, 122–3 (1946) (through *Chem. Abstr.* **41**, 4926*c* (Aug. 10, 1947)).

The treatment of air-dry wool with a dilute solution of NaOH in organic solvents, followed by acidification, produces woolen goods with less tendency to shrink on laundering.

Text. Research J. Oct. 1947

Coating Resins

Survey of methods for testing coating resins. John J. Bradley, Jr. *Official Digest Federation Paint & Varnish Production Clubs* No. **266**, 162–76 (1947) (through *Chem. Abstr.* **41**, 5337*e* (Aug. 20, 1947)).

The survey and suggestions for methods needing improvements are made for rosin and rosin esters, alkyd resins, urea resins, phenol resins, vinyl resins, and government specifications.

Text. Research J. Oct. 1947

Wet-Finishing Equipment

Modern advances in textile wet-finishing equipment. E. Cannity. *Can. Text. J.* **64**, 41–52 (Mar. 21, Apr. 18, 1947).

A discussion is given of the machines used and the advantages of continuous straight-line operation in raw wool preparation and wet finishing of woolen and worsted piece goods. The list of raw-wool operations is comprised of scouring, washing, and drying. Soaping, fulling, washing, tenter drying, automatic controls, and carbonizing machinery are subjects discussed for piece goods. J. A. Woodruff

Text. Research J. Oct. 1947

FIBERS: YARNS: FABRICS: MECHANICAL PROCESSES

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Acetate Staple

Problems and present status of acetate staple-fiber production. Wolfgang Gruber. *Reichsamt Wirtschaftsausbau* Prüf-Nr. **54** (PB 52006), 71–8 (1940) (through *Chem. Abstr.* **41**, 5302*i* (Aug. 20, 1947)).

Descriptive article containing extensive comparative data on the physical properties of cotton, viscose staple fiber, wool (*I*), and acetate staple fiber (*II*). *I* and *II* resemble each other very closely in many (but not all) properties. Gruber alludes to a series of testing methods for gaging the usefulness of textile fibers given by Böhringer (*C.A.* **26**, 1448) and Schieber (*C.A.* **34**, 3096[3]) but no references are given. Beechwood pulp was used in the preparation of *II*.

Text. Research J. Oct. 1947

Cashmere

Structure and dyeing properties of cashmere. Arthur N. Patterson. *Indian Text. J.* **56**, 1105–7 (Sept. 1946).

The fleece of the Cashmere goat is composed of two types of fiber—the long, straight fiber of the outer coat which provides protection, and the true cashmere fiber of the undercoat known commercially as cashmere noil. On the average, a Cashmere goat provides 8 oz. of fleece from which are obtained about 3 to 5 oz. of noil. It has an average length of 1½ to 3 in., and an average diameter of 14 to 16 microns; the coarser noil fibers are 28 microns in diameter. The average diameter of the fiber in the fleece form varies from 14 to 95 microns with about 10% of the fibers greater than 33 microns in diameter. The beard hair appears black, straight, and coarse, and may be round or oblong in cross-section, with a large medulla. The noil fiber is round and free from medullation. Cashmere noil and wool fibers are distinguished by the size and shape of scales, the wool fiber having more scales per inch; also, the scales of the majority of wool fibers project more beyond the fiber shaft than do the cashmere noil scales. Metachrome and top-chrome colors are generally used for dyeing cashmere. The closed kier or pressure-type dyeing machine is preferred. R. K. Worner

Text. Research J. Oct. 1947

Glass Fibers

The properties of textile fiber glass. Paul August Koch. *Reichsber. Chem.* **1** (Prüf-Nr. 015) (PB 52025), 182–92 (1944); cf. *C.A.* **39**, 165[4]; **40**, 7543[3] (through *Chem. Abstr.* **41**, 5269*c* (Aug. 20, 1947)).

Methods and proposed methods for the evaluation of glass threads are discussed.

Text. Research J. Oct. 1947

Properties of Staple Fiber

Problems applying to the improvement of staple fiber. H. Rath. *Reichsamt Wirtschaftsausbau* Prüf-Nr. **54** (PB 52006), 95–101 (1940); cf. *C.A.* **38**, 874[1] (through *Chem. Abstr.* **41**, 5303*h* (Aug. 20, 1947)).

A descriptive article which deals with the effects of various artificial resins, oils, etc., on the degree of swelling, shrinkage, strength on washing, absorptivity, dry and wet strength, etc. Bar graphs are given.

Text. Research J. Oct. 1947

Dimensional Stability

Shrinkage and dimensional stability in rayon fabrics. J. G. Williams. *J. Text. Inst.* **37**, P116–19 (June 1947).

The dimensional instability of fabrics is said to be caused by faulty designing, unskilled production, or

imperfect finishing. The effects of variations in pressing methods are shown. A study is given of the extensions of fabric when subjected to increasing relative humidity. Crimp in the yarn in the fabric is said to affect directly the dimensional stability. J. A. Woodruff
Text. Research J. Oct. 1947

MISCELLANEOUS

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Indian Bast Fibers

Practical utilization of Indian bast fibers other than jute. S. C. Mody. *Indian Text. J.* **57**, 731–3 (May 1947).

The cultivation, harvesting, properties, and uses of flax, ramie, and hemp are briefly described. All of these fibers are available in quantity in India. R. K. Worner
Text. Research J. Oct. 1947

Glass Textiles

Glass fibers and fabrics. C. S. Jones. *Indian Text. J.* **57**, 339–40 (Jan. 1947).

A brief review of the history, production, and uses of glass textiles.
Text. Research J. Oct. 1947

Nylon Hose

Factors in the production of nylon hose. A. R. Munden. *J. Text. Inst.* **38**, 156–60 (Apr. 1947).

Each step in the preparation of the yarn and in the manufacture of the hose is given a practical discussion. Considerable reference is made to observations of operations in America. J. A. Woodruff
Text. Research J. Oct. 1947

Plasticizers and Second-Order Transition Points

Effect of plasticizers on second-order transition points of high polymers. R. F. Boyer and R. S. Spencer. *J. Polymer Sci.* **2**, 157–77 (Apr. 1947).

A review.
Text. Research J. Oct. 1947

Surgical Sutures

Silk and cotton in surgery. Waldemar Schweisheimer. *Indian Text. J.* **57**, 341–2 (Jan. 1947).

Applications of silk, nylon, and cotton for surgical sutures are briefly reviewed. R. K. Worner
Text. Research J. Oct. 1947

Terylene

Terylene. The new British fiber. Anon. *Silk J. Rayon World* **23**, 32–5 (Jan. 1947).

A picture and word story of the development of Terylene.
Text. Research J. Oct. 1947

Color Vision

Color vision in textile industry. W. Schweisheimer. *Indian Text. J.* **57**, 459–60 (Feb. 1947).

A review of the color discrimination tests conducted by J. Tiffin and H. S. Kuhn on about 7,000 workers and reported in *Arch. Ophthalmol.* **28**, 851–7 (1942). R. K. Worner
Text. Research J. Oct. 1947

Infrared Drying

Radiant heat in textile drying. Narhari H. Shah. *Indian Text. J.* **56**, 1016–20 (Aug. 1946).

"The advantages of infrared gas and electric burners in drying textiles are discussed from practical and theoretical viewpoints in relation to water evaporation, operating speed, and fuel consumption."
Text. Research J. Oct. 1947 R. K. Worner

New Finishes

New finishes. F. L. Barrett. *J. Text. Inst.* **38**, 145–54 (Apr. 1947).

A comprehensive review under the following headings: mechanical finishes, effects obtained by chemical modification of the fiber structure, and finishes produced by the fixation in or on the fiber of a suitable assistant. J. A. Woodruff
Text. Research J. Oct. 1947

Silk Production in India

Silk production in India. S. Sutton. *Silk J. Rayon World* **23**, 42–4, 49 (Oct. 1946); 48, 50, 53–4 (Dec. 1946).

A general survey, written in 1945. The quality of Indian silk, organization of the industry, and need for encouragement, improvement, and expansion are discussed.
Text. Research J. Oct. 1947 R. K. Worner

Silkworm Diseases

Silkworm diseases: Their root cause and preventive measures. V. M. Appadhorai Mudaliar. *Indian Text. J.* **57**, 57–63 (Oct. 1946).

Five diseases of silkworms are considered—namely, flacherie, macilenza, pebrine, grasserie, and muscardine. Previous publications on the subject have been mostly in the Italian, French, and Japanese languages. R. K. Worner
Text. Research J. Oct. 1947

Textile Training

Textile education and training conference. *Silk J. Rayon World* **23**, 34–9 (Oct. 1946); 57–8 (Dec. 1946).

Abstracts of the following papers are presented: Technical education for the textile industry, P. F. Burns, pp. 34–5; Standards in National Certificate course, W. E. Morton, pp. 36–9; Textile college equipment and accommodation, H. Bromiley, pp. 38–9 (Oct.); pp. 57–8 (Dec.).
Text. Research J. Oct. 1947 R. K. Worner

PATENT REFERENCES

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Adhesive Fabrics

Pressure-sensitive adhesive fabrics. Gelu Stoeff Stamatoff (to E. I. du Pont de Nemours & Co.). U. S. 2,413,931 (Jan. 7, 1947).

An article patent covering pressure-sensitive adhesive fabrics. Various formulations are covered, all of which contain polyvinyl butyral resin. A. R. Martin
Text. Research J. Oct. 1947

Crimped Viscose Fibers

Production of rayon. William Frederick Underwood (to E. I. du Pont de Nemours & Co.). U. S. 2,413,123 (Dec. 24, 1946).

Crimped viscose fibers are produced by extrusion into a setting bath of pH 5–6.5 which contains specified amounts of sodium bisulfite, sodium sulfite, and sodium sulfate. The filaments are taken up at about ¼ the speed of extrusion, stretched 150%, and then regenerated and dried in a relaxed form.

Text. Research J. Oct. 1947 A. R. Martin

Crimped Filaments

Method of producing regenerated cellulose textile material. William Hale Charch and William Frederick Underwood (to E. I. du Pont de Nemours & Co.). U. S. 2,414,800 (Jan. 28, 1947).

Filaments having a spontaneous crimp-producing capacity are produced by wetting crimped filaments of rayon and drying under tension to remove the crimp. The original crimp reappears when the yarn is wetted subsequently. A. R. Martin

Text. Research J. Oct. 1947

Protein Fibers

Artificial fibers from globular and fibrous proteins. Oskar Huppert. U. S. 2,413,501 (Dec. 31, 1946).

An article-of-manufacture patent covering a fiber consisting of an alkyl-benzene-sulfonic acid salt of a pseudothiohydantoin substituted in position 3 by a protein radical selected from the group consisting of phospho-proteins, globulins, and prolamines. A specific claim covers the use of casein as the protein radical. A. R. Martin

Text. Research J. Oct. 1947

Rayon Spinning

Spinning process. Francis Bernard Cramer (to E. I. du Pont de Nemours & Co.). U. S. 2,412,969 (Dec. 24, 1946).

A process of producing a delustered rayon without the use of pigments. The viscose spinning bath contains a quaternary ammonium hydroxide—e.g., trimethyl benzyl—and the yarn is spun into a coagulating bath consisting of mixed salts at a salt concentration of 25–40%. The pH of the bath is between 3 and 7, and the temperature is about 55°C. The coagulated viscose is subsequently stretched and then regenerated in a relaxed state to permit shrinkage.

Text. Research J. Oct. 1947 A. R. Martin

Fabric Finishes

Dressing fibrous and textile materials. Leon Lilienfeld (to Lilienfeld Patents, Inc.). U. S. 2,422,572 (June 17, 1947).

A process of finishing a textile fabric by treatment with an alkaline solution of a degraded cellulose derivative. 39 claims cover the process of finishing, the finished textile as an article of manufacture, and various processes for preparation of the degraded cellulose materials.

Text. Research J. Oct. 1947 A. R. Martin

Xanthated cellulose derivative and process of coating with same. Leon Lilienfeld (to Lilienfeld Patents, Inc.). U. S. 2,422,573 (June 17, 1947).

Similar to 2,422,572 but covering the use and preparation of xanthates of degraded cellulose derivatives. 19 claims. A. R. Martin

Text. Research J. Oct. 1947

Shrinkproofing Wool

Process for shrinkproofing wool. Maurice Leslie Ward (to E. I. du Pont de Nemours & Co.). U. S. 2,414,704 (Jan. 21, 1947).

A process of shrinkproofing wool by treatment at pH 1 to 3 in an aqueous solution of 1,3-dichloro-5,5-dimethylhydantoin. A. R. Martin

Text. Research J. Oct. 1947

Water-Repellent Treatment

Process for finishing textile materials, particularly to render the same water-repellent. Ernst Zerner, Gertrude D. M. Davies, and Peter I. Pollak (to Sun Chemical Corp.). U. S. 2,413,024 (Dec. 24, 1946).

Cellulosic textiles are rendered water-repellent by treatment with such chemicals as di-heptadecyl-beta-napthylamine anile in Stoddard solvent and subsequently drying and curing the treated fabric at 130–150°C. Claims cover use of chemicals of the general class, $R_1R_2C{=}NR_3$, where R_1 and R_2 are alkyl radicals containing at least 8 carbon atoms and R_3 may be alkyl or aryl. A. R. Martin

Text. Research J. Oct. 1947

Textile treating compounds containing silicon and the process of making same. Charles A. MacKenzie (to Montclair Research Corp.). U. S. 2,415,017 (Jan. 28, 1947).

A water-repellent treatment for cellulosic textiles claimed to be fast to both laundering and dry-cleaning. The treating solution is the reaction mixture resulting from heating stearamide, silicon tetrachloride, paraformaldehyde, and pyridine in dioxane solution at 90°C.

Text. Research J. Oct. 1947 A. R. Martin

Cotton Chopper

Cotton chopper. Charles Frederick Callahan. U. S. 2,414,507 (Jan. 21, 1947).

A cotton chopper adapted for use with conventional tractors.

Text. Research J. Oct. 1947 A. R. Martin

Drafting Mechanism

Drawing mechanism for textile slivers. Ramón Balmes Solanas. U. S. 2,422,444 (June 17, 1947).

A drawing mechanism for spinning frames. This is an improvement relating to U. S. patent 2,205,701 (June 25, 1940). Invention consists essentially of a conducting roller that makes contact with the bottom rolls of 2 consecutive pairs of drafting rolls, and a traversing device for the roving that is synchronized with the movement normally given to the roving by spinning machines. A. R. Martin

Text. Research J. Oct. 1947